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ION EXCHANGE COLOR AND MINERAL REMOVAL FROM KRAFT BLEACH WASTES

Robert L. Sanks

Montana State University

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Ion Exchange Color and Mineral Removal from Kraft Bleach Wastes

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Laboratory evaluations of twenty resins and seven carbons for removing color and minerals from a four-stage kraft bleach plant showed resins were equal to carbon for decoloring the combined waste. With few exceptions, resins were unsuited for decoloring wastes from each stage separately. Except for success in the use of weak wash to regenerate Amberlite XAD-8 resin, utilization of mill liquors for regeneration was unsuccessful. Sulfuric acid, caustic, and ammonia were good regenerants, but lime was poor.

Single stage ion exchange produced water adequate for unbleached pulping. Two-stage desalination produced water adequate for bleached pulping. Any of the continuous counter-current ion exchange processes are probably adequate for producing water for bleached pulping.

The estimated cost for desalination including amortization over a 10 year period at 9 percent interest, labor, chemicals, maintenance, and repairs are estimated to vary from $1.38/1000 gal (for the non-optimized process used in the laboratory) to $0.42/1000 gal (with estimated 90 percent cation regeneration efficiency, 85 percent anion regeneration efficiency, and 87 percent product recovery). (EPA)

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ION EXCHANGE COLOR AND MINERAL REMOVAL FROM KRAFT BLEACH WASTES

by

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ABSTRACT

Twenty resins and seven carbons were evaluated in the laboratory for the removal of color and minerals from the four-stage kraft bleach plant waste of the Hoerner Waldorf Corporation.

Resins were equal to carbon for decoloring ditch waste (the combined waste of the bleach plant). With a few exceptions, resins were unsuited for decoloring wastes from the chlorine, hypochlorite, and chlorine dioxide stages. Except for success in the use of weak wash to regenerate Amberlite XAD-8 resin, attempts to utilize mill liquors for regenerating resins were unsuccessful. Sulfuric acid, caustic, and ammonia were good regenerants, but lime was poor.

Single stage ion exchange with starvation regeneration produced water adequate for unbleached pulping. Two-stage desalination produced water adequate for bleached pulping. Any of the continuous countercurrent ion exchange processes are probably adequate for producing water for bleached pulp manufacture.

The estimated cost for desalination by ion exchange including amortization over a 10 year period at 9 percent interest, labor, chemicals, maintenance, and repairs are estimated to vary from $1.38/1000 gal (for the non-optimized process actually used in the laboratory) to $0.42/1000 gal (with estimated 90 percent cation regeneration efficiency, 85 percent anion regeneration efficiency, and 87 percent product recovery).

This report was submitted in fulfillment of Project 12040 DBD under the sponsorship of the Water Quality Office, Environmental Protection Agency in cooperation with the Department of Civil Engineering and Engineering Mechanics, Montana State University.

Key words: bleach plant waste, ion exchange, desalination, color removal, cost.

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SECTION I
CONCLUSIONS

After pretreatment by massive lime precipitation, water desalinated by a single stage, strong acid exchanger followed by a weak base anion exchanger is adequate for use in the manufacture of the unbleached pulp. Excluding pretreatment, storage, and hook-up of the ion exchange units to the rest of the mill the cost was estimated to vary from $1.38/1000 gal to $0.42/1000 gal. The larger cost was based on duplication of laboratory conditions in full scale operation namely: 75 percent acid regeneration efficiency, 84 percent caustic regeneration efficiency, 3 BV of rinse, no recovery of regenerants, and a resin life of two months. With optimization to increase regeneration efficiency and to decrease the rinse volume, this cost can be substantially reduced. Assuming a Progressive Mode ion exchange system, 87 percent regeneration efficiency, sulfuric acid for regenerating cation resins, ammonia for regenerating anion resins, 1.3 BV of rinse, 87 percent product recovery, a one year resin life and amortization over 10 years at 9 percent interest, the cost was estimated to approximate $0.49/1000 gal of product water. If the aggressiveness of the bleach plant waste (85 percent chlorination and 15 percent caustic extraction stage effluents) can be reduced by pretreatment to increase the useful life to five years for cation resins and three years for anion resins, the cost was estimated to approach $0.43/1000 gal. The cost of single stage strong acid-weak base ion exchange could, perhaps, be reduced to $0.42/1000 gal but the quality of the product water would be inferior to the product from a Progressive Mode system. The prices for chemicals used in these cost estimates are April, 1973 prices actually paid for chemicals delivered to the Hoerner Waldorf Mill at Frenchtown, Montana. The cost of ammonia, however, was conservatively estimated by a local supplier, but no doubt this chemical could be obtained at a lower cost.

Although every effort was made to ensure reasonable cost estimates with a lack of bias, more accurate cost estimates depend upon extended operations of large pilot plants at the mill site where pretreatment, 24-hour operation, and procedures which can be realized in practice can be maintained. Nevertheless, the cost of ion exchange is competitive with reverse osmosis and deserves further study for improving the quality of bleach plant wastes and to achieve closed systems.

The most pressing problems requiring further research are: (1) reduction or elimination of the aggressiveness of the wastes, (2) integration of regenerating chemicals into the mill process, (3) inexpensive recovery or disposal of concentrated wastes from the ion exchange plant, (4) development of new resins more resistant to attack, (5) optimization in the selection and operation of necessary pretreatment methods, (6) optimization of ion exchange with respect to selection of system and its operation, (7) careful consideration for the integration of other processes including reverse osmosis, carbon sorption, and the use of newly-developed ion exchange processes for pretreatment, and (8) elimination of slime, foaming, and corrosion problems.

The best resins were approximately equal to the best activated carbon for the removal of color from ditch waste, the composite waste consisting of 15 percent caustic extract and 85 percent chlorination stage wastes from the bleach plant. The best sorbents were weak base porous resins with phenolic matrices. While resins generally performed well with ditch waste and caustic extract stage wastes, they performed poorly with waste from chlorination, hypochlorite, and chlorine dioxide stages. By contrast, carbon performed better on chlorine, hypochlorite, and chlorine dioxide stage wastes than on caustic or ditch waste. These observations do not apply to Amberlite XAD-2 nor XAD-8 as no data on color sorbency curves were obtained for them. Later tests indicated XAD-8 was effective for sorption of color from ditch waste.

Of those anion resins tested for color removal from ditch waste, the best appeared to be Duolite A-6, a weak base resin with secondary amine functional groups on a phenolic matrix. The second best resin was Duolite A-7 which is a similar but less expensive resin.

The small amount of color remaining in the product of single stage desalination of ditch waste could not be removed at neutral pH either with phenolic resins or with carbon. But residual color was effectively removed by phenolic resin at pH 3 (obtained by adding acid or by further decationization).

Of the regenerants tested, hydrochloric acid, sulfuric acid, and sodium hydroxide produced excellent results, ammonia was good, lime was poor, and white liquor was very poor. At a concentration of 5 percent sulfuric acid, calcium sulfate precipitated in the column, but the difficulty disappeared when the acid concentration was reduced to 3 percent. Ammonia appeared to be about 80 percent as effective as caustic, but with operation optimized for ammonia regeneration, Sanks and Kaufman (1965) were able to achieve nearly 90 percent regeneration efficiency in fixed-bed ion exchange. Regeneration with white liquor produced rapidly declining capacities caused by calcium carbonate precipitation in the resins. When treated with hydrochloric acid, large quantities of gas evolved, and the resin was restored to virgin capacity. However, a regeneration process which requires daily renovation of resin seems impractical.

Optimum rates of flow vary markedly for different resins. In general, optimum rates of flow for service and for regeneration are considerably higher than those listed by manufacturers whose literature pertains to the production of high quality water. Optimization for flow rate should include considerations of leakage, efficiency, and amortization of capital because high flow rates result in fewer or smaller reactors. The required rinse volumes for desalination practice is much less than rinse volumes listed by resin manufacturers. In general, service flow rates can be very high, regenerant flow rates may be optimum at 20 to 30 BV/hr, and rinse at 1.3 BV (10 gal/cu ft) has been found adequate.

Ditch waste from the Hoerner Waldorf Mill was apparently abnormal because the pH was usually above 5 whereas, according to Button (1972) the pH of the effluent from most bleach plants is less than 3. The lower pH of wastes at other mills would enhance the removal of color by resins.

Ion exchange resins and resin sorbents offer considerable promise for aid in producing closed water systems in pulp manufacture. Several new and superior resins have recently become available including Amberlite XAD-8 and an improved version of Duolite A-6. New processes have recently been developed with better integration into mill processes such as the regeneration of Amberlite XAD-8 with weak wash and the process described by Anderson, Broddevall, and Lindberg et al (1973) in which the resin is regenerated with black liquor which is then burned in the recovery furnace. The integration of processes such as these with desalination by ion exchange might remain the cheapest means of achieving closed systems.

SECTION II
RECOMMENDATIONS

As the cost of ion exchange appears to be competitive with the cost of reverse osmosis, both at the present time and potentially, more research effort is recommended for ion exchange. At the present time much research effort is now being lavished upon reverse osmosis whereas comparatively little is being devoted to ion exchange. The results of this investigation and of other new products and processes in ion exchange are encouraging.

It is recommended that additional investigations be made concerning reduction of the aggressiveness of bleach plant wastes toward resins. Such efforts should include basic research to develop a means for predicting the aggressiveness of waters because the only method now available is the time-consuming "life" tests.

When a satisfactory means for reducing aggressiveness of waters has been developed to extend resin life to approximately a year or more, a large scale pilot plant should be constructed with reactors one to two feet in diameter. These must be versatile enough to permit a wide range of residence times and flow rates in each reactor or each part of reactors. The pilot plant should permit a continuous countercurrent ion exchange process or a close approximation thereof. Satisfactory processes would include: Chem-Seps, Graver CCIX, and Progressive Mode. Whichever process is selected, it should be readily possible to make field alterations of residence times, flow rates, and distribution of time for service, regeneration, and rinse. Optimization for regenerant flow rates, rinse volume, reduction of waste, and pretreatment (especially for particulate matter) should be studied long enough to ensure successful prototype operation over extended periods of time.

The use of inexpensive regenerants such as ammonia, weak wash, and white liquor, should be studied together with possible recovery and reuse, integration into other mill processes, or at least innocuous disposal methods.

The tendency of investigators and government agencies to limit research to one process should be rejected and replaced by a philosophy of considering all processes and combinations of processes. A team consisting of experts in ion exchange, reverse osmosis, and pulp mill practice and chemistry is needed.

SECTION III

INTRODUCTION

HISTORY OF ION EXCHANGE

Although there are early references to phenomena that might be construed to have been ion exchange, the discovery of ion exchange is attributed to Thompson (1850) who in 1847 discovered that ammonium sorbed on soil could not be eluted with water. Investigating Thompson's discovery, Way (1850) determined the phenomenon was (1) an exchange of equivalent ions, (2) a function of concentration, (3) less effected by temperature than other types of chemical reactions, and (4) a function of selectivity.

The first commercial application of softening by ion exchange was promoted by Gans (1905), and the development of synthetic cation and anion zeolites by Adams and Holmes (1935) made demineralization by ion exchange possible. The modern era of ion exchange began with the invention of synthetic resins by d'Alelio (1944) and only a decade later the annual sales of ion exchange products reached $40 million. After another decade there were approximately 17,000 ion exchange plants. Because many firms now manufacture ion exchange products, equipment and systems are highly competitive, much of it is so standardized that it can be obtained virtually "off-the-shelf."

In the early sixties, ion exchange was used mostly for water softening and the production of demineralized water of high quality principally for boiler feed. A small proportion of the synthetic resin production was used for production of pharmaceuticals, decolorization of sugar, and other industrial purposes. The production of high quality water required thorough regeneration and extensive rinsing so the use of ion exchange for the partial demineralization of brackish waters could not be justified by desk-top analyses due to the extensive portion of the water produced required for rinsing and regeneration. It was generally conceded ion exchange could be dismissed as impractical for the demineralization of high solids water unless the regenerants could somehow be recovered for reuse or unless the resins could be regenerated by some method of heat exchange or the use of electrical current. Early in that decade, however, several workers applied themselves to the demineralization of high solids water, notably Kunin, Higgins, Odland and Pabich, the Asahi Chemical Corporation, and Sanks and Kaufman.

Desal Process

The Desal Process developed by Kunin (1965) typically utilizes a 3-bed system containing weak-electrolyte resins. In the first bed, Amberlite IRA-68 resin (in bicarbonate form) exchanges influent chlorides and sulfates in raw water for bicarbonate. The second exchanger, Amberlite IRC-84 (in hydrogen form) exchanges influent cations for hydrogen ions. In the last exchanger, IRA-68 (in hydroxyl form) the bicarbonate is exchanged for hydroxyl ions and the water is consequently demineralized. The first reactor is regenerated to the hydroxyl form with caustic, ammonia, or lime, and the second reactor is regenerated to the hydrogen form with sulfuric acid. The third reactor is left in its exhausted state which is the bicarbonate form. Hence, at the beginning of the second cycle, the position of the exchangers is reversed with respect to right and left, and raw water enters the "third" reactor first. Several modifications, such as a 2-reactor system, are possible. Kunin and Downing (1970) estimated an operating cost of $0.20/1000 gal to produce potable water from a brackish water containing 1000 mg/l of total dissolved solids in a 1 mgd plant for a capital cost of $250,000.

Chem-Seps Process

Higgins (1964) explained the use of a continuous, moving bed ion exchange process for demineralizing high solids water. The resin in the reactor is confined to a closed loop divided by butterfly valves into separate reaction sections: (1) loading or exhaustion, (2) feed-rinse, (3) rinse elimination, (4) regeneration, (5) regeneration-rinse, and (6) second water elimination. At frequent intervals the resin is pulsed a few inches around the loop countercurrently to the solution flow. By means of ports and conductivity probes, mixed liquor at the liquid interfaces is eliminated to prevent contamination of the product. Its advantages are: the last of the resin contacted by the influent feed is fully regenerated and only fully exhausted resin is regenerated. The system permits high flow rates limited only by pressure drop. Higgins (1965) proposed nitric acid for regenerating cation resin and ammonia for regenerating weak base anion resin. Thermal decomposition of the nitrate salts in the spent cation regeneration can be utilized to recover nitric acid and metallic hydroxides. Ammonia can be evolved by reacting the spent anion regenerant with the metallic hydroxides. Efficiencies of regenerant reclamation varied from 50 to 80 percent in laboratory tests. The overall efficiency of the process with respect to chemical regeneration can be 95 percent or more.

Sul-biSul Process

In the Sul-biSul process evaluated in the field by Schmidt et al (1969) cation removal is accomplished conventionally, but anions are removed by a strong base exchanger operating between the sulfate form and the bisulfate form. During exhaustion the anion bed is converted to the bisulfate form by the acidic influent. It is regenerated to the sulfate form with either raw water or lime. Its capacity is only half the capacity of a conventionally operated ion exchanger, but regeneration is cheap, and the strong base electrolytes are not subject to fouling by organic materials. Odland and Pabich (1965) made extensive analyses of costs required to demineralize high solids water. For example, a 1 mgd plant could remove 1500 mg/l from water containing 2000 mg/l total dissolved solids at a cost of approximately $0.56/1000 gal.

Graver CCIX Process

The Graver CCIX Process is a fully automatic continuous countercurrent ion exchange process which uses three reactors for cation exchange and three more for anion exchange. Service or exhaustion is carried out in the first column. At intervals, the influent feed is halted for 30 seconds and the exhausted horizon of resin is pumped to the second column for regeneration. The fully regenerated horizon of resin in the second column is pumped to the third column for rinsing. During this 30 second interval, resin in the first column drops downward in the reactor and rinsed resin from the third column is pumped into the top of the reactor through a special valve. All of the reactors operate with an upward flow of liquid. The first reactor always has a freshly regenerated horizon of resin to polish the feed water. As with the Chem-Seps method invented by Higgins, the Graver CCIX Process utilizes regenerant at very high efficiency according to Levendusky, Limon, and Ryan (1965).

Progressive Mode

As explained by Adams (1970), the Progressive Mode system (marketed by The Permutit Company) utilizes three or more reactors each for cation and for anion exchange. The reactors are regenerated and rinsed in place and in a sequence such that the feed water first contacts partly exhausted resin in one reactor and finally leaves a last reactor full of freshly regenerated resin. The advantages of progressive mode are: each reactor is of the simple type that has been commonly used for at least the last 30 years, and a wide variety of flow regimes coupled with operational flexibility can be used to accomplish almost any desired effluent quality at high efficiencies of chemical regeneration.

Simple Fixed Bed Systems

Working with the simplest ion exchange system (a strong acid cation exchanger followed by a weak base anion exchanger) Sanks and Kaufman (1966) optimized the exchange cycle to produce low solids water from 2000 TDS feed at higher chemical efficiencies than those previously reported.

Acid efficiencies of 93 percent were obtained by a combination of reutilizing partly spent regenerant and by "starvation" regeneration. Regeneration efficiency decreased to 80 percent when only fresh acid was used. However, by adding a layer of weak acid resin on top of the strong acid resin, Sanks (1967) found the efficiency of regeneration using fresh acid only could be increased to 92 percent. Abrams and Poll (1967) termed it the "Duo-Cat" Process. It is effective only when the proportion of bicarbonate ion exceeds 20 percent of the total anions. Efficiencies of weak base resins were 89 percent using caustic and 86 percent using ammonia. Sanks and Kaufman found it cost $0.15/1000 gal in a 10 mgd plant to remove 350 mg/l of total dissolved solids from sewage treated by activated sludge, coagulation, sand filtration, and carbon sorption. They experienced no difficulty with blinding or irreversible sorption.

Fouling and Blinding

The effects of organics in blinding strong-base ion exchange resins and the difficulty of renovating them has been studied by Wilson (1959) and others. Using many radio-active labeled compounds, Ward and Edgerley (1965) studied the role of various functional groups in blinding strong-base resins. The mechanism and kinetics of poisoning was discussed by Olson (1968).

Countercurrent Regeneration

Countercurrent regeneration is universally known to be much more efficient than concurrent regeneration. But Lux (1971) pointed out slight shifts in the resin bed, due to counter-flow conditions, reduced efficiency. In the Econex process, inert granular synthetic material in the plenum keeps the resin bed firmly in place and improves regeneration efficiency. Some of the inert material is pumped out of the plenum for backwashing.

Summary of Federal Programs

By the end of 1966, a considerable body of knowledge had been developed on the desalination of high solids water by ion exchange. The Advanced Waste Treatment Research Program of the Public Health Service was initiated in 1960 to alleviate growing water pollution problems and to renovate wastewater for direct reuse or recycling. The Advanced Waste Treatment Research Program was transferred to the Environmental Protection Agency which is now striving for "closed" systems in water use by industries. The advancements in ion exchange have lead to the inclusion of this process for evaluation in this program.

PULP INDUSTRY

The pulp industry is the fifth largest industry in the United States. Kraft pulp accounts for the largest tonage of any process. Large quantities of water are required for this process and particularly for the bleaching of kraft pulp. Not only is the quantity of water required for bleaching large (15,000 to 60,000 gallons per ton of bleached pulp) but the bleach waste is by far the most highly colored and objectionable of all the liquid wastes discharged from a kraft plant. Furthermore, it contains high total dissolved solids, a fairly high COD, a moderate BOD, and it possesses a moderately high toxicity.

Reuse

The reuse of water in the pulp industry is increasing. Cooper (1968) showed how more careful housekeeping reduced water use at one plant to 28 percent of its previous amount per ton of pulp. Haynes (1966), reporting on the reuse of water by 10 kinds of pulp and paper mills, showed overall water reuse in 1965 was about 220 percent of total intake. In a more recent TAPPI survey, Haynes (1968) showed the reuse of water to be increasing toward a target figure of 300 to 400 percent. Nelson et al (1972) discussed the possibility of reducing water use to 6000 gal/ton pulp and Yankowski (1972) proved (by laboratory tests confirmed by mill tests) it was possible to reduce bleach wash water by 50 percent with no effect on brightness of pulp. Factors inhibiting reuse are (in order of their importance): slime, suspended solids, color, dissolved solids, foaming, corrosion, and scale. Berger (1966) stated advanced treatment of kraft mill waste will become common practice before long. Secondary treatment of kraft mill wastes cost more than $1.50 per ton in 1966 and complete treatment (primary sedimentation, biological oxidation, color removal, and sludge disposal) would cost more than $3.00 per ton of production or $0.05/1000 gal assuming 60,000 gal of effluent per ton of production. He stated desirable water quality limits for bleached kraft manufacture are:

Color	5 CU	Alkalinity	75 mg/1 $CaCO_3$
Hardness	100 mg/1 $CaCO_3$	Iron	0.2 mg/1
TDS	250 mg/1	Manganese	0.1 mg/1
Chloride	150 mg/1	COD	8 mg/1
Turbidity	5 JTU	BOD	2 mg/1

Massive Lime Precipitation

In the massive lime precipitation process patented by Berger, Gehm, and Herbet (1964) for color removal the colored waste is mixed with the entire lime budget used to caustisize the green liquor. Transferring the resulting filter cake to the caustisizer, the color bodies dissolve in the white liquor, pass through the digestion process, and are finally burned in the black liquor recovery furnace. The process, fully described by the National Council for Stream Improvement (1962), removes 88 to 95 percent of the color which renders the water suitable for reuse for some plant purposes. Bennett et al (1971) determined the color reduction is due not to sorption but to reaction of lime with very weakly acidic groups to form insoluble calcium salts. Remaining color is attributable to the more soluble calcium salts of low molecular weight. A more extensive discussion of this work is given by National Council for Air and Stream Improvement, Inc. (1970). Interstate Paper Corporation (1971) found it possible to reduce color from the effluent of an unbleached linerboard mill to 125 CU with only 1000 mg/l of lime, which is a much smaller dose than that used for massive lime precipitation.

Color sorption. The potential use of granular carbon to polish the waste effluents after massive lime precipitation has been given by McGlasson, Thibodeaux, and Berger (1966). Rimer, Calahan, and Woodward (1971) estimated costs for carbon sorption of combined municipal and pulp mill effluents. The mechanism, effectiveness, and cost analysis of carbon sorption were the subject of intensive study by the National Council for Stream Improvement (1965, 1967), and the council concluded carbon should be used as a polishing agent only after massive lime precipitation.

Many other studies of sorption might well apply to decoloring bleach plant effluents. The West Virginia Pulp and Paper Company (1969) recommended mixed pulverized carbons for sorption over a wide range of molecular sizes. Recovery and regeneration of powdered carbon poses difficult problems which are yielding to current research efforts. A promising technique is the manufacture of carbon by "scorching" black liquor, using the carbon to sorb color from wastes, then burning sorbed organics and carbon for heat recovery.

Dickinson and Barrett (1969) found finely divided sorbents consisting of polar resins, activated carbon, and inorganic sorbents mutually enhance and complement one another for removal of color and haze. Rebhun and Kaufman (1967) concluded the performance of resinous sorbents was comparable to carbon for sorbing color from treated wastewaters. However, virgin carbon was nearly twice as effective as virgin resins for sorbing gross organic material.

Rohm and Haas Company (1970) developed a sorbent resin XAD-2 which was intended to polish pulp mill effluents after massive lime precipitation. By using white liquor for regeneration, the process can be integrated into the mill process in which the color bodies are eventually burned in the recovery furnace. Later, Rohm and Haas Company (1971) found a more effective sorbent, XAD-8, had sufficient capacity to remove color from raw bleach wastes and the color could be eluted with weak wash. Unfortunately, their literature did not mention the pH must be less than 2.5 for effective sorption nor that concentrated eluants like white liquor are too strong for effective regeneration.

Ruzickova (1970) found Ostion-SL(L-33), a weakly basic gel-type Czechoslovakian anion exchanger obtained by condensation of aromatic amines with formaldehyde, to be suitable for decoloring sulfite mill wastes, sulfate mill wastes, and bleaching wastes after biological treatment. The resin was also able to remove residual phosphates.

Desalination for Reuse

Desalination of the bleach wastes can be accomplished by many processes, among them: reverse osmosis, electrodialysis, and ion exchange. Pilot plant studies of reverse osmosis have been reported by Wiley, Ammerlaan, and Dubey (1967) who found it possible to concentrate solids to 10 g/liter or more and to obtain high yields of colorless, non-foaming product water. In a later work, Ammerlaan, Lueck, and Wiley (1968) reported difficulty with the fouling of membranes. Wiley, Dubey, and Ba[illegible]l (1972) concluded membrane replacement, required at least once per year, represented 60 to 80 percent of the operating costs and commercial application would depend upon success in attaining membrane life far beyond present limitations.

Thibodeaux and Berger (1967) found the Desal process effective in desalinization of caustic stage bleach and further studies by Thibodeaux and Wright (1970) led to cost estimates of 60.4¢/1000 gal to reduce TDS from 2500 mg/l to 25 mg/l. The fixed capital investment was estimated at $1,280,000 for six 20 ft ID x 15 ft high columns, regenerant tanks, and pumps. Regenerants were one percent solutions of sulfuric acid (for the IRC-84 resin) and ammonia (for the IRA-68 resin).

OBJECTIVES

Relatively little attention has been given to the use of resins as sorbents. Although resins are more expensive than carbon and although they can be blinded, poisoned, or oxidized under some conditions, they can be regenerated in situ with cheap chemicals and with little or no loss in capacity. Their kinetic properties are equal to or better than those of carbon, their capacities are high and their properties can be varied and controlled by the manufacturer. Resins can be used to sorb organics and to reduce dissolved solids at the same time.

General Objectives

The general objectives were to determine the economic potential of synthetic resins for the control of pollution from kraft bleach wastes particularly in reuse and recycle systems. It includes the investigation for the removal of color, other organics, and dissolved minerals from the waste streams of kraft bleach mills and an estimate of the economics for comparison with other methods.

Specific Aims

The specific aims were:

1. to determine the relative merit of various resins and carbons by determination of sorption isotherms,
2. to optimize fixed bed ion exchange for the removal of color and for demineralization combined with color removal,
3. to verify the best types of resins for sorption and demineralization,
4. to seek more economical methods and chemicals for regeneration,
5. to investigate acceptable means of waste regenerant disposal, especially methods which permit reuse of chemicals,
6. to compare sorption and ion exchange using resins with other methods for renovating water,
7. to estimate the cost of treatment by resins alone or in conjunction with other methods, and
8. to establish criteria for the design and operation of a pilot plant.

SCOPE

The study was limited to the investigation of commercially available resins only and to the bleach waste from one kraft pulp plant. Only the simplest ion exchange system (strong acid cation exchange and either strong or weak base anion exchange) was to be considered so the results could be as universally applicable as possible.

The work was divided into the following phases: exploration, color sorbency in columns, ion exchange, life tests, and economic evaluation. The exploratory tests were designed to establish operating procedures and to make a preliminary evaluation of each resin which would result in eliminating all but the most favored resins for further investigations.

PROPRIETARY PRODUCTS

Manufacturers and trade names are listed with reluctance and a warning. Disguising the names of resins places an undue hardship on the reader with respect to interpreting results. The mention of trade names in no way constitutes either endorsement or rejection of a product. A slight change in feed water analysis can make a great deal of difference in the life or efficiency of a resin, and the reader is cautioned that the results reported herein might not apply to another waste under other conditions.

SECTION IV
EQUIPMENT

ION EXCHANGE

Pilot Plant

To facilitate laboratory operations, such as the collection of fractions, ending a run at a precise value of color, pH, or conductivity breakthrough, switching from downflow to upflow, etc., two semi-automatic pilot plants shown schematically in Figure 1 were constructed. The columns were Corning double-tough Pyrex conical glass pipe. Top and bottom sections were separated by a central distributor which permitted rapid draining of the plenum or block flow (compressed-bed upward flow). Liquids were carried in 1/4 x 1/8 R3603 Tygon (vinyl) tubing connected to the column with Swagelok double-end-shut-off quick-connects (labeled QC) made of 316 stainless steel. They permitted instant switching of feed, waste, and drain hoses to either bottom, center, or top of the column. The components are described in Table 1.

Control of breakthrough. The conductivity meter was altered by the installation of a rise-fall switch connected to a separate manual-reset relay box. The wiring diagram for the relay is shown in Figure 2. This apparatus makes it quick and easy to stop the feed pump on a rise or on a fall of conductivity to any preset value from 10 to 10,000 micromhos/cm^2.

The Sargent recorder was modified so it can also shut off the pump motor at any predetermined value of pH, color, or any other quantity that can be monitored by the Hitachi Perkin Elmer M-139 spectrophotometer. A large washer was clamped to each of the two chart pen drive wheels in such a manner as to allow its rotation to any position. A pin welded

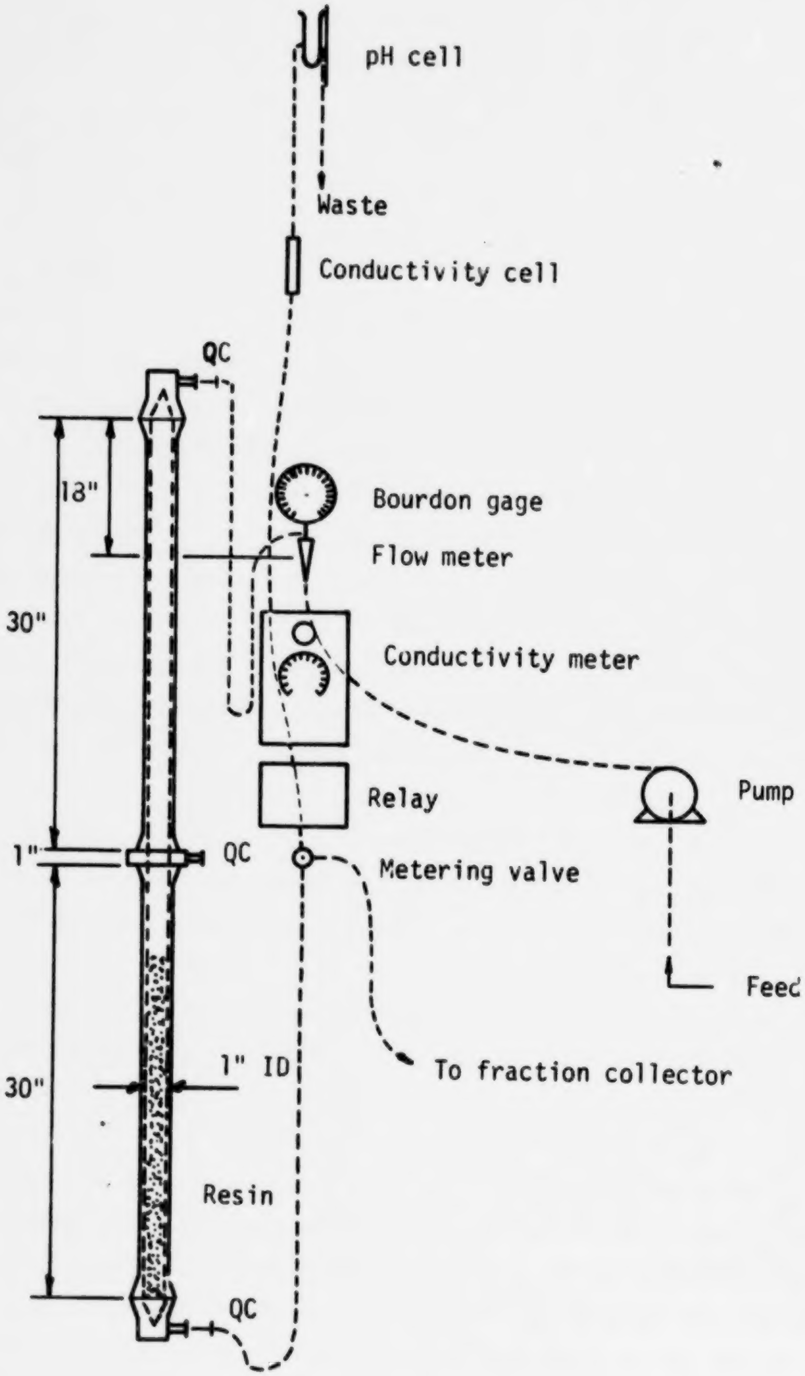

pH cell
Waste
Conductivity cell
QC
18"
30"
Bourdon gage
Flow meter
Conductivity meter
Pump
Relay
1"
QC
Metering valve
Feed
1" ID
To fraction collector
30"
Resin
QC

FIGURE 1. SCHEMATIC DIAGRAM OF ION EXCHANGE PLANT

TABLE 1

COMPONENTS OF ION EXCHANGE PLANTS

Part	Description
pH electrode	Sargent S-30072-15 combination, glass
Conductivity cell	Beckman JD-2. K = 2.00
QC (Quick Connect)	Swagelok 400-1/4QC-200 DESO 316
Bourdon gage	US Gage 19001
Flowmeter	Fischer Porter 10A3135M
Conductivity meter	Beckman RE104-Y11 Solu Bridge
Relay	Advance 964 D54 with manual reset
Metering valve	Nupro SS-4MX with micrometer handle
Fraction collector	Isco Golden Retriever 326
Pump	Sigmamotor T-65, Bodine 54SH DC motor and Minarik 76 SH Controller
Not shown in Figure 2:	
pH meters	Sargent DR and Orion 404
Recorder	Sargent dual channel DSRG equipped with two Micro JV26 microswitches
Spectrophotometer	Hitachi Perkin-Elmer M-139 equipped with a flowthrough cell

to each washer is used to trip the microswitch which carries electric current to the pump motor. When the pen reaches a preset position on the chart, the microswitch is activated which stops the motor. Two channels can be operated simultaneously and independently.

Small Columns

Half-inch ID columns were used for screening tests in order to conserve the limited quantities of wastewater. They were made from heavy wall Pyrex glass tubing two feet long. End closures were rubber stoppers ground to fit and bored for a short tube to fit the rubber tubing. A

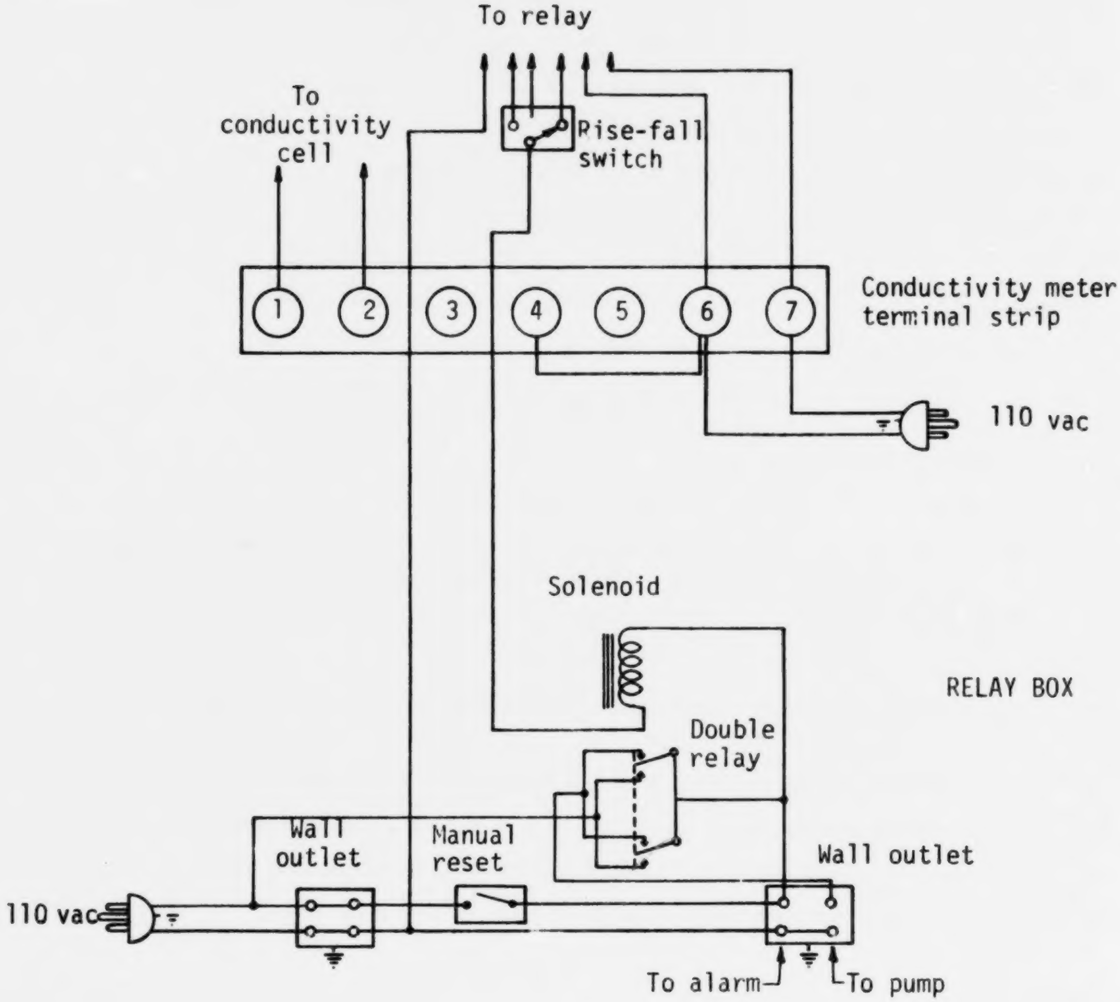

To relay
To conductivity cell
Rise-fall switch
1
2
3
4
5
6
7
Conductivity meter terminal strip
110 vac
Solenoid
RELAY BOX
Double relay
Wall outlet
Manual reset
Wall outlet
110 vac
To alarm
To pump

FIGURE 2. CIRCUIT DIAGRAM FOR ION EXCHANGE PLANT AUTOMATIC SHUT-OFF DEVICE

tuft of glass wool supported the resin bed. The feed was placed in a five gallon plastic jug pressurized to 3 psi with compressed air. A manifold of rubber hose and glass tees led to five half-inch columns operated simultaneously. Flow rate, regulated by Hoffman hose clamps, was measured with a stopwatch and a small graduated cylinder.

Appurtenant Equipment

Shakers. Batch tests for isotherms were carried out in 250 ml erlenmeyer flasks containing 100 ml of liquid agitated in a Blue M Model MSB1122 A-1 water bath shaker holding 10 flasks. Preliminary tests showed the optimum amplitude to be one and one half inches and the optimum speed 112 rpm. The temperature of the flasks was maintained between 17 and 20°C. To augment the limited capacity of the Blue M water bath shaker, a special shaker was constructed to hold 54 flasks. It consisted of a 20 gage galvanized iron tray mounted on a 3/4 inch angle iron frame to which four roller skate wheels were attached. The tray was driven by a connecting rod attached at a radius of 3/4 inch to the pulley of a Bodine motor. It was crude but effective and reliable.

Environmental cabinet. Most tests were conducted at room temperature maintained between 68 and 75°F. Elevated temperature tests were conducted in a custom made environmental cabinet 6'3" high by 6'8" long by 2'10" deep inside dimensions. The temperature controller, built especially for this cabinet, maintained any given temperature within ± 1°C.

LIFE TESTS

Ion Exchange Reactors

Sixteen ion exchange reactors were made of Corning double tough conical Pyrex pipe reducers specially fabricated to have a one-inch ID section 3 1/2 inches long expanding to 1 1/2 inch ID with an overall length of 7 1/4 inches. They were fitted with standard aluminum flanges and gaskets with end closures made of lucite fitted with nylon Swagelok tubing connections. The resin was supported by 80 mesh stainless steel screens. All tubing was 1/4" x 1/8" Tygon R3603 tubing connected to a nest of plastic tees in such a way so that the total length of inlet or outlet to each column was the same.

The combination of upflow operation and the larger diameter above the resin bed completely prevented any plugging of resin columns. The apparatus was quite successful.

Pump

A sixteen channel roller pump similar in concept to the Sage Model 375 Peristaltic pump was constructed especially for the project. It was powered by a Bodine NSH-11D3 variable speed reversible motor controlled by a Minarik SL14P converter-controller equipped with a 10-turn helipot. The unit can be set for any speed between 3 and 44 rpm with an error of less than 1 percent.

The tubing in the pump was silastic rubber 1/4" OD by 1/8" ID. By stretching each tube as needed, it was easy to regulate the flow within 1 percent of the desired value.

As first constructed, the pump tended to cut certain of the rubber tubes badly. The pump was remodeled by removing the hinges and holding the cover with four vertical threaded studs and by widening the pressure plates by gluing to each plate a strip of Teflon sheet wide enough to reduce gaps to a minimum. No further trouble occurred and no tubing ever again required replacement.

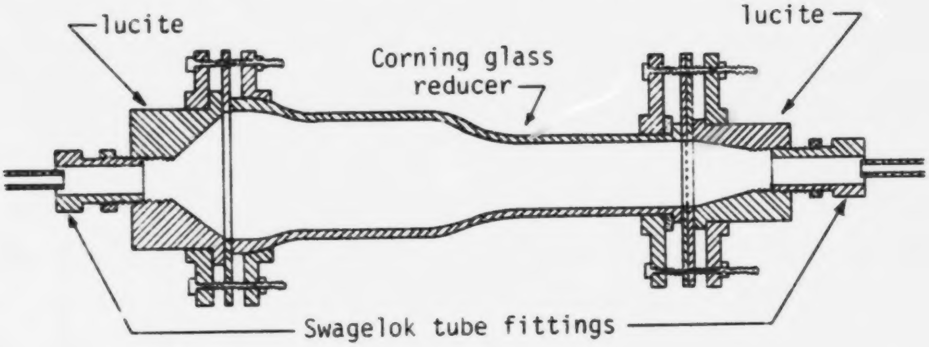
Automatic Cycler

The automatic cycler consisted of a Cramer type 540 timer in a custom chassis. Four 3-way switches were provided to override the timer switches for control. The timer switches activate Asco Catalog no. 826206 stainless steel solenoid automatic valves. The four valves were connected respectively to: (1) the acid storage tank, (2) pretreated bleach plant waste, (3) caustic storage tank, and (4) cation reactor product water.

The apparatus is shown schematically in Figure 3. Essentially it consisted of two separate systems: one for cation exchangers and one for anion exchangers. One of the automatic valves failed after a few hours of operation and required replacement. Otherwise the apparatus worked perfectly without attendance save tor the necessity of refilling the tanks with liquor.

CHROMATOGRAPHY

The chromatographic column was a Pharmacia type K9/60, 9 mm in diameter and 60 cm long. The flow of the eluent, 0.02 molar NaCl, was maintained at 10 ml/hr by a Sage Model 375 tubing pump. Fractions were collected in an Isco Golden Retriever Model 326 fraction collecter.


lucite
lucite
Corning glass reducer
Swagelok tube fittings

COLUMN DETAILS

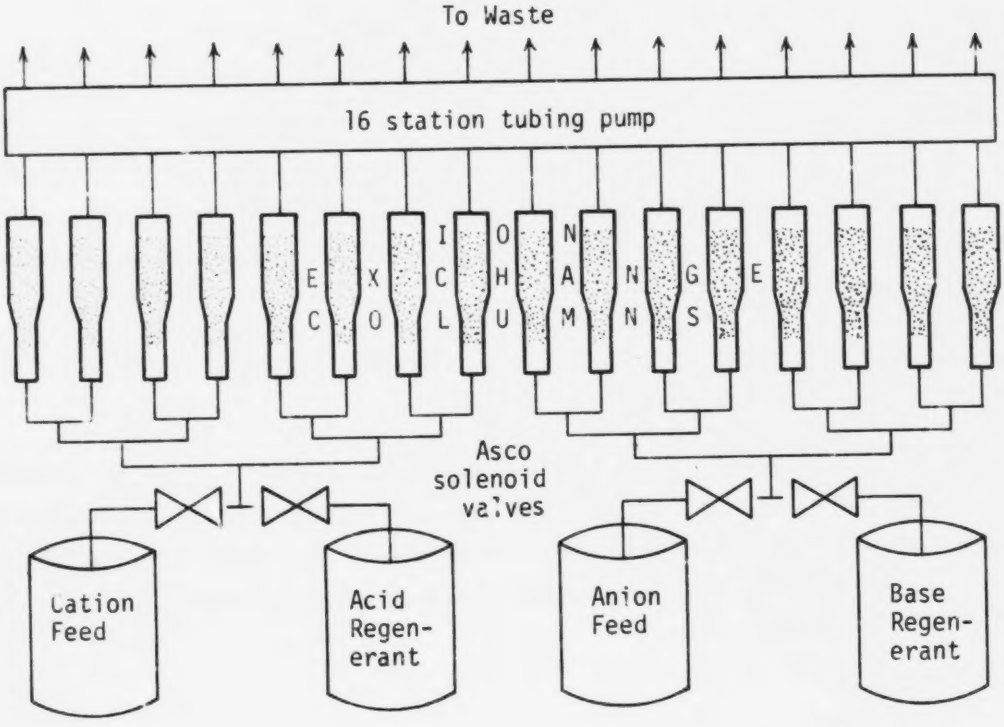

To Waste
16 station tubing pump
ION EXCHANGE COLUMNS
Asco solenoid valves
Cation Feed
Acid Regenerant
Anion Feed
Base Regenerant

FIGURE 3. SCHEMATIC DIAGRAM OF 16-STATION ION EXCHANGER

ANALYTICAL EQUIPMENT

Spectrophotometer

Color was measured with an Hitachi-Perkin Elmer Model 139 spectrophotometer at a wave length of 422.2 mμ and at a slit width of 0.32 mm. The spectrum is continuous and varies slowly, so a wave length of 420 mμ would give essentially the same results. Because the concentration of color varied greatly, cells with effective light paths of 10 cm, 1 cm, and 0.036 cm were used. The effective light path 0.036 cm, used to avoid tedious dilution, was made by placing a polished lucite block with an effective thickness of 0.964 cm into the 1 cm cells. The unit was calibrated with several colored solutions to insure accuracy, repeatability, and conformance with the standard 1 cm cell.

Sodium and potassium. The M-139 spectrophotometer was fitted with a flame photometer for measuring sodium at a wave length of 589 mμ and a slit width of 0.01 mm and potassium at a wave length of 768 mμ and a slit width of 2.0 mm. The photo-multiplier was connected to a Sargent Model SLRG 10-inch strip chart recorder for precise determination of average photometer response.

Carbon Analyzer

During all of the preliminary investigations, total organic carbon was measured with a Beckman carbonaceous analyzer belonging to another department and operated by the personnel of that department. The instrument was out of commission so much of the time that most of the organic carbon measurements could not be made. During the last part of these investigations, total organic carbon was measured on a new Beckman Model 915 Total Organic Carbon Analyzer, an instrument which gave reliable results.

Amperometric Titrater

Due to the difficulty of titrating highly colored solutions with color indicators, a Wallace and Tiernan Amprometric Titrater was obtained for the measurement of chlorine. It functions independently of color and measures total residual chlorine at pH 4 and free available chlorine at pH 7. As determined by iodometric titration, the accuracy was found to be satisfactory.

pH Meters

Several meters were used to measure pH including an Orion Model 404 Ionalyzer, a Beckman Zeromatic II and a Sargent Model DR. All were equipped with combination electrodes. Calibrations were made frequently and always with solutions within 3 pH units of the unknown solution.

SECTION V
MATERIALS

RESINS AND CARBON

Carbon was used in these investigations only to provide comparison in color sorbency with synthetic resins. All sorbents and ion exchangers are described in Table 2.

TABLE 2
SORBENTS EVALUATED

Designation		Functionality	Porosity	Composition	
Name	No.			Matrix	Active group
Cation resins					
Dowex	HCR-W	Strong Acid	Gel[a]	Polystyrene	SO_3Na
Duolite	C-25D	Strong Acid	Porous[a]	Polystyrene	SO_3Na
Amberlite	IRC-84	Weak Acid	Gel[a]	Acrylic	COOH
Amberlite	IRC-50	Weak Acid	Gel[b]	Methacrylic	COOH
Amberlite	IR-120+	Strong Acid	Gel[b]	Polystyrene	SO_3Na
Anion resins					
Dowex	11	Strong Base	Gel[c]	Polystyrene	$N(CH_3)_3Cl$
Dowex	WGR	Weak Base	Gel[d]	Epoxy-amine	NR_2
Amberlite	IRA-93	Weak Base	Macro-reticular[b]	Polystyrene	NR_2
Amberlite	IRA-402	Strong Base	Gel[b]	Polystyrene	$N(CH_3)_3Cl$
Amberlite	IRA-68	Weak Base	Gel[b]	Acrylic	NR_2
Duolite	A-6	Weak Base	Macro-porous[c]	Phenolic	NR_2
Duolite	A-7	Weak Base	Macro-porous[c]	Phenolic	NR_2
Duolite	A-57	Weak Base	Gel[a]	Epoxy-amine	NR_3Cl

(Table 2 Continued)		Porosity	Matrix	Active group
Sorbents				
Amberlite XAD-2	Sorbent	Gel[a]	--	--
Amberlite XAD-8	Sorbent	Macro-reticular[e]	--	--
Duolite S-37	Weakly Basic	Macro-porous[c]	Phenolic	NR_2
Duolite ES-33	Weakly Basic	Macro-porous[c]	Phenolic	NR_2
Duolite S-30	Sorbent	Semi-porous[c]	Phenolic	ØOH
Filtrasorb 100	Sorbent	Porous[h]	Carbon	Carbon
Filtrasorb 200	Sorbent	Porous[i]	Carbon	Carbon
Filtrasorb 300	Sorbent	Porous[f]	Carbon	Carbon
Filtrasorb 400	Sorbent	Porous[g]	Carbon	Carbon
Nuchar WV-L	Sorbent	Porous[f]	Carbon	Carbon
Nuchar WV-G	Sorbent	Porous[g]	Carbon	Carbon
Nuchar WV-W	Sorbent	Porous[g]	Carbon	Carbon

[a] mesh size 20 x 50
[b] mesh size 16 x 50
[c] mesh size 14 x 50
[d] mesh size 20 x 40
[e] mesh size 20 x 60
[f] mesh size 8 x 30
[g] mesh size 12 x 40
[h] mesh size 8 x 20
[i] mesh size 12 x 30

PROCESS STREAMS

All wastewaters were originally obtained from the Hoerner Waldorf kraft pulp mill located at Frenchtown, near Missoula and 236 miles from Bozeman.

Hoerner Waldorf Mill

The mill was constructed in 1957 and expanded in 1960 and again in 1966. It now produces 900 tons per day of kraft paper board or unbleached pulp and between 130 and 150 tons per day of bleached pulp. The species of wood utilized varies but all are soft woods.

Pulping

All bleached pulp is produced in batch digesters. Each of the eight digesters holds a 10 ton charge on a dry basis (20 tons wet as loaded) and the total capacity is 60 3-hour cooks per day for a gross ultimate capacity production of 600 tons per day. However, 150 tons of pulp (dry basis) is the maximum that is actually bleached. All flow diagrams and all chemical usages are figured on the basis of a 150 day production of bleached pulp.

Bleaching

The bleaching process, shown schematically in Figure 4, consists of four stages: (1) chlorination, (2) caustic extraction, (3) sodium hypochlorite, and (4) chlorine dioxide. The flow diagram in Figure 5 shows extensive countercurrent reuse of water so that the only waste produced by the plant is 2930 gpm from the chlorination washer, 460 gpm from the caustic washer, other small sporadic flows due to leakage in wash-down operations and it may also contain some black liquor. The flows do not always balance exactly. The discrepancies are thought to be due to leaky valves.

Chemical Inventory

The chemical inventory and the chemical purchases for the bleach plant on a daily basis for 150 tons per day are given in Table 3. Those for the rest of the entire plant are given in Table 4.

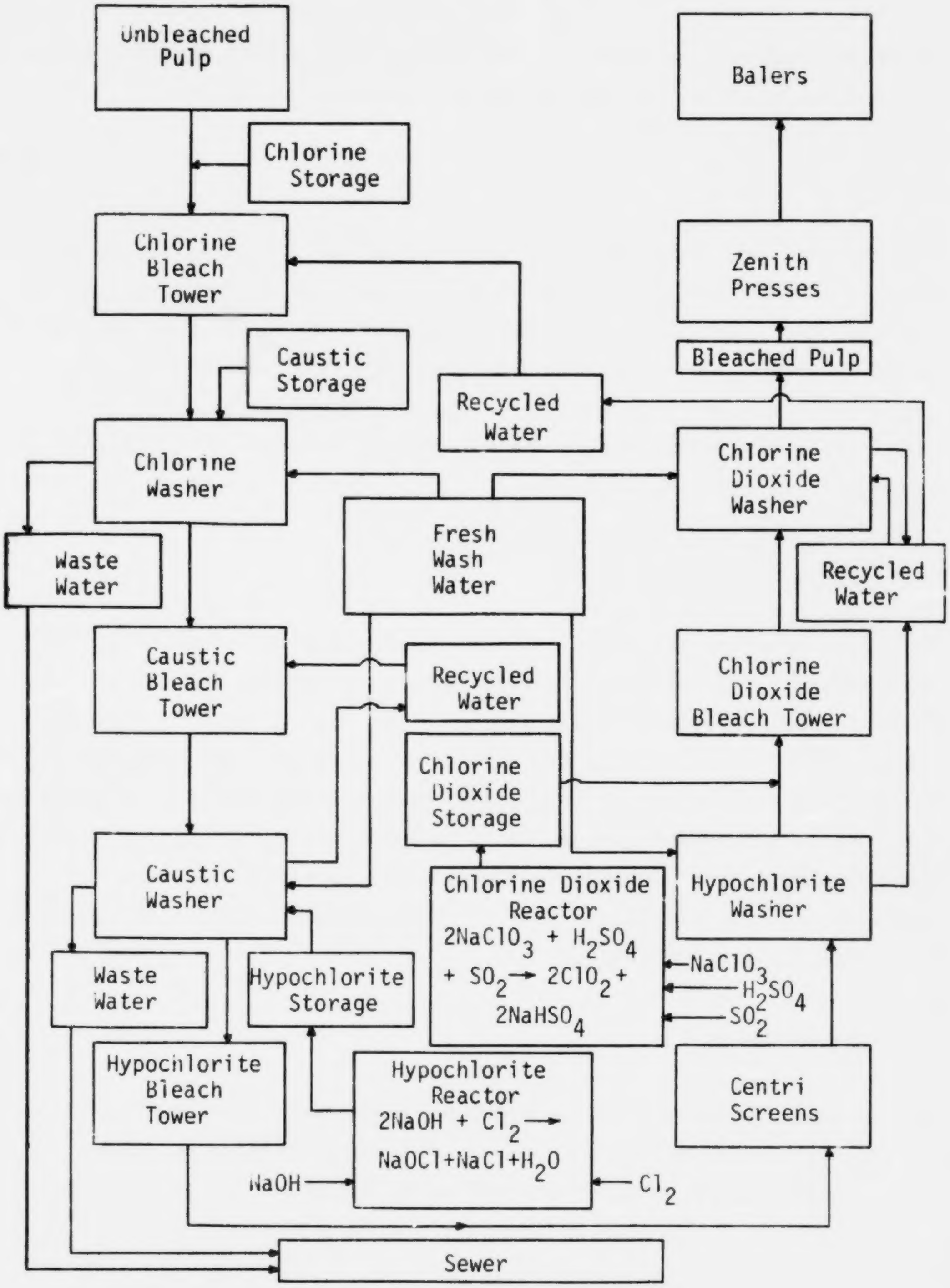
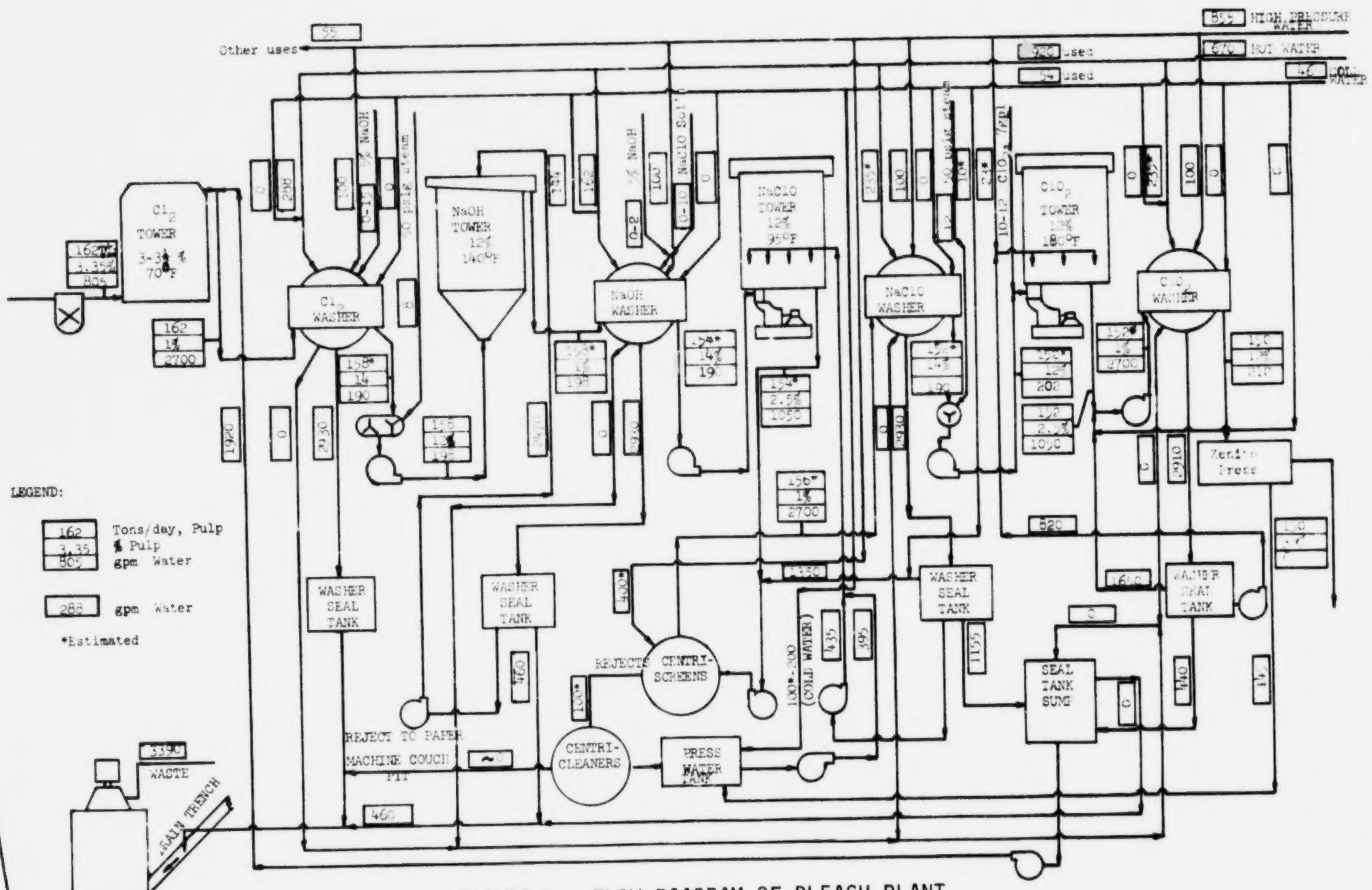

Unbleached Pulp
Chlorine Storage
Chlorine Bleach Tower
Caustic Storage
Chlorine Washer
Waste Water
Caustic Bleach Tower
Recycled Water
Caustic Washer
Waste Water
Hypochlorite Storage
Hypochlorite Bleach Tower
Hypochlorite Reactor
$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$
NaOH
Cl_2
Sewer
Fresh Wash Water
Recycled Water
Chlorine Dioxide Storage
Chlorine Dioxide Reactor
$2NaClO_3 + H_2SO_4 + SO_2 \rightarrow 2ClO_2 + 2NaHSO_4$
$NaClO_3$
H_2SO_4
SO_2
Centri Screens
Hypochlorite Washer
Chlorine Dioxide Bleach Tower
Recycled Water
Chlorine Dioxide Washer
Bleached Pulp
Zenith Presses
Balers

FIGURE 4. SCHEMATIC BLEACH PLANT FLOW DIAGRAM.



HIGH PRESSURE WATER
HOT WATER
COLD WATER
Other uses
used
Cl2 TOWER 3-3½% 70°F
Cl2 WASHER
NaOH TOWER 12% 140°F
NaOH WASHER
NaClO TOWER 12% 95°F
NaClO WASHER
ClO2 TOWER 12% 180°F
ClO2 WASHER
% NaOH
NaClO Sol'n
90 psig steam
10-12 ClO2 #/pl
Zenith Press
WASHER SEAL TANK
SEAL TANK SUMP
CENTRI-SCREENS
CENTRI-CLEANERS
PRESS WATER TANK
REJECTS
REJECT TO PAPER MACHINE COUCH PIT
100*-200 (COLD WATER)
WASTE
DRAIN TRENCH
LEGEND:
Tons/day, Pulp
% Pulp
gpm Water
gpm Water
*Estimated

FIGURE 5. FLOW DIAGRAM OF BLEACH PLANT

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TABLE 3
CHEMICALS IN BLEACH PLANT
(Based on 150 tons bleached pulp per day)

Chemical	Usage Conc.	Storage Conc.	Usage[a] tons/day	Cost, \$/ton[b] fob	Freight	Total
Chlorine, as Cl_2	--	100%	13.65	54.50	14.00	68.50
Caustic, 50% Na_2O	5%	50%	9.75	56.25	11.20	67.45
Sulfuric acid as H_2SO_4	93.6%	93.6%	0.68	17.47	7.90	25.37
Sodium chlorate	96%	96%	0.98	--	--	143.40
SO_2 as SO_2	--	100%	1.12	--	--	68.72
Pitch dispersant[c]	--	--	--	--	--	771.40

[a] fiscal year November 1968-September 1969

[b] April 1973

[c] Vanzak 112, R. T. Vanderbilt Co. Inc., 230 Park Avenue, New York, NY

TABLE 4
CHEMICALS IN ENTIRE PLANT EXCEPT BLEACH PLANT
(Based on 1000 tons unbleached pulp per day)

Chemical	Usage Conc.	Storage Conc.	Usage[a] tons/day	Cost, \$/ton[b] fob	Freight	Total
Salt cake, as Na_2SO_4	98%	98%	61	16.50	12.50	29.00
Caustic, 50% Na_2O	5%	50%	35.5	56.25	11.20	67.45
Spent caustic as Na_2SO_4	100%	100%	1.0	--	--	25.00
Lime, as CaO	95%	95%	15.5	16.00	14.20	30.20
Bulk Starch	100%	100%	39.5	101.40	9.00	110.40
Alum, 17% Al_2O_3	50%	50%	39.0	--	--	63.35
Sulfuric acid as H_2SO_4	93.6%	93.6%	20.0	17.47	7.90	25.37

[a] fiscal year November 1968-September 1969 [b] April 1973

Lime

The capacity of the three lime kilns is 290 tons CaO/day although the plant is usually operated at 250 tons/day. The lime is slaked and reacted with 800 gpm of green liquor (equivalent to 52 g/l). If massive lime precipitation were practiced and the maximum lime output of the mill were slaked with the 460 gpm wasted from the caustic washer seal tank, the lime dose would equal 105 g/l. If all the 3390 gpm of ditch waste were to be precipitated with the 290 tons lime/day, the dosage would be 14.2 g/l.

Bleach Wastes

During the early part of the investigations, the characteristics of the ditch waste varied considerably and upset the results of the experiments. Hence, an "artificial" ditch waste was manufactured by combining 15 percent caustic extract with 85 percent chlorine waste. Direct comparisons of ditch waste and artificial ditch waste showed close agreement, an example of which is indicated in Table 5. Only pH, suspended solids, and total alkalinity are greatly different. These differences can be accounted for by floor sweepings from the lime kiln area which are present in ditch waste but not in artificial ditch waste. In October 1970, the waste collection piping system of the Hoerner Waldorf Mill was combined with waste from the paper machines so it was no longer possible to obtain unadulterated bleach plant wastes. All subsequent experiments were, perforce, made with the artificial ditch waste. The maximum and minimum values of the various parameters which characterize the wastes are given in Table 6.

Liquors from the bleach plant were transported to Bozeman in plastic containers. During the investigations for batch tests, the liquors were stored at 4°C in a refrigerator. Low temperature storage for

TABLE 5

COMPARISON OF DITCH AND ARTIFICIAL DITCH WASTES

	Type of Waste	
Characteristic	Ditch Waste 7/31/70	Artificial Ditch Waste 15% caustic extract, 85% chlorine waste 7/31/70
pH	9.4	5.4
Suspended solids, mg/l	500	22
TDS, mg/l	1690	1490
Color		
CU, orig. pH	2820	2730
CU, pH 7.6	2420	3170
Total Alkalinity, mg/l as $CaCO_3$	570	44
COD, mg/l	415	550
Residual free chlorine, mg/l	0	40
Jar Test:		
% color removed	88	92.5
CaO, mg/l	1200	1200
Specific conductivity μmhos/cm^2	2340	1990
TOC, mg/l	270	250

TABLE 6
CHEMICAL ANALYSES OF ARTIFICIAL DITCH WASTES AFTER PRETREATMENT

Cation	Concentration, me/l		Anion	Concentration, me/l	
	max	min		max	min
Na	24.0	16.8	HCO_3	7.0	4.1
K	tr	tr	Cl	23.1	13.6
Ca	6.9	4.8	NO_3	0.03	tr
Mg	tr	tr	SO_4	2.7	1.4
TDS (Computed), mg/l				2157	1700

large quantities of liquor needed for column runs was quite impractical. Furthermore, the characteristics of liquors stored at room temperature did not change sufficiently to affect test results.

Anion Feed

Feed to the anion column is the effluent from the cation column either with or without decarbonation. If the effluent from the cation column is to be carbonated, the decarbonation tower would normally discharge into an intermediate reservoir. Hence, feed to the anion column would consist of a mixed, uniform cation effluent. To expedite the preparation of anion feed, a two-inch diameter cation column 24 inches deep was operated to 35% breakthrough of the sodium ion. The product was mixed by sparging until the CO_2 concentration was reduced to 2 mg/l, which required approximately two hours. A typical analysis of the decarbonated cation product water is shown in Table 7.

TABLE 7
TYPICAL ANALYSIS OF ANION EXCHANGER FEED WATER
Effluent from 2-inch column, decarbonated

Cation	Concentration me/l	Anion	Concentration me/l
H	9.9	H_2CO_3	0.1
Na	3.1	Cl	13.2
Ca	0.0	NO_3	tr
Mg	0.0	SO_4	0.1
	13.0	S	tr
			13.4

pH = 2.0

REGENERANTS

Acid

Regenerant for pilot plant cation exchange was technical grade sulfuric acid. Difficulty with calcium sulfate precipitation using 5 percent acid was elminated by reducing the concentration to 3 percent. Hence, resin was regenerated with 3 percent acid.

To avoid difficulty with calcium sulfate precipitation in life tests in which the columns operated automatically, 1 N hydrochloric acid was used for regeneration.

Base

Several bases were used to regenerate sorbents and anion exchangers: 1 N technical grade sodium hydroxide, 4 percent NH_4OH, and white liquor. The concentration of white liquor (equivalent to caustic) is kept at 3.0 N by the Hoerner Waldorf Mill. When it was necessary to use a lower concentration, the white liquor was diluted with Bozeman tap water. Bozeman tap water is essentially a calcium carbonate water with little sodium, chloride, or sulfate, and the dissolved solids content varies from 60 to 110 mg/l. The chemical analysis of white liquor is given in Table 8.

TABLE 8
CHEMICAL ANALYSIS OF WHITE LIQUOR

Cation	Concentration me/l	Anion	Concentration me/l
Na	4000	OH	2100
K	100	CO_3	785
Mg	1.0	Cl	5.4
Ca	0.7	S	900
Sum	4101.7	SO_4	94
		Sum	3884.4
	Error:	5.5%	

TDS (Computed): 216,700 mg/l

pH: 13.3

Dilute specific conductivity: 781,000 µmhos/cm^2

Weak wash is essentially a dilute form of white liquor. Whereas white liquor contains about 6.2 lbs Na_2O/cu ft, weak wash contains only 0.5 lbs Na_2O/cu ft. Table 9 is an analysis given by Weeks (1972).

TABLE 9
WEAK WASH COMPOSITION

Constituent	Concentration, lb/cu ft
Active Na_2O	0.5
Total alkali	1.0
$NaOH$	---
Na_2S	---
Na_2CO_3	---
$Ca(OH)_2$	saturated
Na_2SO_4	tr

CHROMATOGRAPHY

Chromatographic separations were carried out with Sephadex G-10 and Bio-Gel P-2, 100 to 200 mesh. The eluant was 0.02 N sodium chloride, Baker Analyzed reagent grade. The gel was calibrated with a mixture of Dextran Blue (molecular weight ≃ 5000) and potassium ferricyanide (molecular weight = 329).

SECTION VI
LABORATORY PROCEDURES

EXPLORATORY TESTS

Isotherms in Batch Tests

All anion resins were presoaked for 30 minutes to cause the beads to swell. About a liter was backwashed with tap water in a 2-in. ID x 6 ft column at a rate sufficient to cause 60 percent bed expansion and the fine debris was allowed to wash out of the column. After draining to an inch above the top of the resin column, two bed volumns of 1 N NaOH were passed downward at a rate of 12 BV/hr followed the same flow rate by a rinse of 5 BV of tap water. This was followed by a 1 N HCl acid treatment with the same volumes, flow rates, and rinses. The entire cycle was repeated again and then the resin was converted to free base form with 2 bed volumes of 1 N NaOH followed by a distilled water rinse to pH 8. Resins exhibiting much swelling during conditioning (such as Duolite A-57 and S-33) were regenerated upflow to prevent undue pressure within the glass column.

Cation resins were cycled in the same way except the sequence of acid and base was reversed.

Duolite S-30 sorbent resin was treated like the anion resins except: the concentration of NaOH was 2 percent, the concentration of HCl was 1 percent, and the last treatment with NaOH was omitted leaving the resin neutralized with acid. All other sorbent resins were left in the OH form.

The carbons were presoaked approximately 30 minutes, loaded into a 2-inch ID x 6 ft column and backwashed to remove carbon dust. In early tests the carbon granules abraded so much that the turbidity interfered with color measurements. Preshaking the carbon in distilled water to remove sharp edges was unsuccessful and the carbon continued to abrade. Turbidity caused by carbon dust was removed by pressure filtration through a 0.45 μ filter in a Millipore filter syringe converted to filter by pressure rather than by suction.

Samples of liquors were prepared for sorbency testing by filtration through a Whatman No. 30 filter paper and by pH adjustment to 7.6 ± 0.1. Acidic samples were neutralized with 1.5 N NaOH. Basic samples were neutralized with 8 N and 0.1 N HCl for early tests and later with gaseous CO_2. An initial color measurement was made on the filtered liquor (neutralized to pH 7.6 before the start of each run. Several concentrations of sorbents were used for each isotherm run, usually 0.1, 0.25, 0.5, 0.75, 1.0, 2.5, and 5.0 grams (wet, drained weight) per 100 ml of liquor. In addition, a blank containing no resin was included for comparison.

Color measurements were taken at 1/2, 1, 2, 4, 8, and 24 hour intervals and thereafter at 24 hour intervals until no further change in color could be observed. But even a period of a week was not always sufficient to achieve true equilibrium.

Color Sorbency in Batch Tests

Sample and sorbent preparation were identical to those used for isotherms except 100 ml of the filtered neutralized waste was added to a 250 ml flask containing 5 grams (wet, drained weight) of the sorbent. The flask was immediately placed in the shaker, and color measurements were taken after shaking 10, 20, and 40 minutes and at 1, 2, 3, and 4 hours after the start. The starting times were staggered to permit 8 or even 10 runs per day with five minute intervals between color readings except at the 2 hour and 3 hour readings when three simultaneous readings were scheduled. These three readings were taken at a total of three minutes, a time span too short to cause significant error.

Pretreatment by Massive Lime Precipitation

Pretreatment consisted of massive lime precipitation followed by two-stage recarbonation. Lime was slaked by adding 5 ml of the liquor being investigated per gram of lime. The mixture was heated on the hot plate until the reaction began. The vessel was removed from the hot plate and the reaction allowed to complete itself, and the contents were then cooled to room temperature before the slurry was used for precipitation.

Precipitation runs were planned so six samples could be started almost simultaneously. The liquor to be pretreated was quickly added to the previously slaked lime to increase the volume to one liter. The samples were immediately placed in position under the stirrer, where they received five minutes of high speed stirring at about 140 rpm to insure complete mixing, and 15 minutes of slow stirring at 50 rpm. Upon completion of the stirring the samples were transferred without delay to one-liter graduated cylinders (liquid height 28 cm) in which the settling rates of the lime solids were timed. After two hours of settling the supernatant liquor was siphoned out of the cylinder, filtered, and kept in tightly stoppered flasks. At this stage aliquots were removed for physical and chemical analyses. Typical analyses are shown in Table 10.

Recarbonation. Recarbonation was performed in two stages. A sample of supernatant liquor was transferred to a 250 ml graduated cylinder, the recarbonater nozzle was placed at the bottom, and the air-CO_2 mixture was introduced at a flow rate of about 450 ml/min. The liquid height was always 28 cm in all experiments. The pH was monitored continuously. The gas flow was stopped when the pH reached 11.5. The settling rate of the calcium carbonate precipitate was timed. After the precipitate was removed by vacuum filtration, the liquid was poured into a second cylinder and the second recarbonation step was continued

TABLE 10

CHEMICAL ANALYSES OF ARTIFICIAL DITCH WASTES AFTER PRETREATMENT
(Lime precipitation and recarbonation to pH 7.6 and 300 CU)

Cation	Concentration me/l	Anion	Concentration me/l
	Collection Date 1/4/71		
Na	24.0	HCO_3	4.1
K	Tr	Cl	23.1
CA	6.9	NO_3	0.03
Mg	Tr	S	Tr
Sum	30.9	SO_4	2.7
		Sum	29.93
	Error:	3.1%	
TDS (computed):	2157 mg/l		
	Collection Date 2/23/71		
All used for color sorbency. No chemical analysis made.			
	Collection Date 4/6/71		
Na	16.8	HCO_3	7.0
K	Tr	Cl	13.6
Ca	4.8	NO_3	Tr
Mg	Tr	S	Tr
Sum	21.6	SO_4	1.4
		Sum	22.0
	Error:	1.8%	
TDS (computed):	1700 mg/l		

to pH 7.6. Chemical and physical analyses were made of the final products.

Storage

Liquors obtained from the Hoerner Waldorf Plant were transported by truck or bus to Bozeman and placed in refrigerators set at 4°C with the least practical delay (8 to 15 hours after collection). The samples from the chlorination, hypochlorite, and chlorine dioxide stages were taken from the caustic washers whereas caustic was taken from the caustic seal tank. The bleach ditch sample was taken from an open ditch about 600 yards from the mill.

After completion of batch tests, the quantities of liquor needed were so large it was impractical to store them in a refrigerator. Therefore, samples were stored at room temperature. Ditch waste and artificial ditch waste were found to be quite stable for several weeks under room temperature conditions.

Gel Permeation Chromatography

The proper gel for fractionation of the kraft bleach wastewater was selected by calibrating with a mixture of Blue Dextran (molecular weight ≈ 5000) and potassium ferricyanide (molecular weight = 330). Of the Sephadex gels, only G-10 gave adequate separations, but Bio-Gel P-2, 100 to 200 mesh appeared to be better for the purpose and most of the results were obtained with it.

One ml of the mixture, or the liquid to be analyzed, was placed at the top of the column and eluted with 0.02 N sodium chloride (Baker analyzed reagent grade). The elution flow rate was 0.166 ml/min regulated by a Sage Model 375 tubing pump. Ten samples/hr were collected by the Isco Model 326 fraction collector until 36 ml of samples (equal to the volume of the column) were collected.

The collected fractions were too small to be tested for color or for sorbency at 265 mμ, so TOC (measured on the Model 915 Total Organic Carbon Analyzer) was used as the concentration parameter for each fraction collected.

The general procedure for gel permeation chromatography has been described by Determann (1968) and Sephadex (1970).

COLOR SORBENCY IN COLUMNS

Feed Preparation

Lime-precipitated waste for column runs was prepared in 50 gallon barrels by adding enough slaked lime to produce 90 percent color removal. After 6 to 12 hours of sedimentation, the supernatant liquor was decanted and recarbonated to pH 11.5, the precipitate was allowed to settle 6 to 12 hours, and the supernatant liquor was again decanted and recarbonated in a second stage to pH 7.6 ± 0.1.

Single Runs on Virgin Resins

Resins were preconditioned with two cycles of acid and base followed by thorough rinsing as described in Exploratory Tests.

Regeneration optimization. Optimization regeneration was begun with preconditioned resins exhausted at a rate of 20 BV(bed volumes)/hr to partial breakthrough with lime-precipitated ditch waste in a 1-inch ID x 24-inch deep bed. Duolite A-6 was exhausted to 90 percent breakthrough whereas Duolite S-37 and Amberlite IRA-68 were exhausted to 30 percent breakthrough. After exhaustion, the resin bed was backwashed, rinsed, removed from the column, and thoroughly mixed. Each bed was divided into 24 packets of 13.1 ml each. Each packet provided a bed 1 inch in diameter x 1 inch deep for regeneration tests.

Each preliminary regeneration test was performed on a fresh packet of 13.1 ml of exhausted resin. The packet of resin was placed in a 3 inch long column 1 inch in diameter and was then backwashed with distilled water. Water was drained to the top of the resin bed. Regenerant was applied downflow to the resin bed at a constantly monitored flow rate of 2.5 to 40 BV/hr. The effluent was collected in numerous successive fractions. Flow was continued until the effluent became almost colorless, which showed that regeneration was essentially complete.

Cyclic Tests

Duolite A-6 and S-37 were the resins selected for color sorbency in cyclic runs. In all cyclic color sorbency runs, the feed was pumped downward through the column at the rate of 20 BV/hr. The resin beds were 1 inch in diameter and 24 inches deep in their regenerated, backwashed, and settled state. Runs were halted at a color breakthrough of 50 percent (150 CU). In all but a few runs this criterion was closely approached.

Regeneration was always countercurrent at an upflow rate of 20 BV/hr. The regenerant was pumped into the bottom of the column and the effluent was removed through a screened port located just above the top of the resin bed (30 1/2 inches above the bottom screen). The feed remaining in the 30 inch high plenum (upper part of reactor) was not disturbed. Samples of the regeneration effluent were collected at one minute intervals for color measurement.

Immediately following regeneration, the resin was rinsed upflow with 5 BV of distilled water. Then the direction of rinse was changed to downflow with 15 BV of distilled water pumped into the column at the middle port.

Two cyclic series of runs were made with: (1) white liquor and (2) technical grade NaOH regenerants. With white liquor as a regenerant, 9 cycles were obtained, after which it was necessary to rejuvenate the resin. No rejuvenation was necessary in the second series of runs in which 1 N technical grade NaOH was used for 15 cycles.

Single runs were made using three different solutions of lime: (1) a saturated solution of lime, (2) a 2 percent lime slurry, and (3) a 4 percent lime slurry. Regenerant at rates of 16 to 20 BV at a rate of 20 BV/hr was passed upflow through the column followed by 10 to 15 BV of distilled water rinse upflow and then 30 BV of distilled water rinse downflow.

In another series of runs, the resin was removed from the column and placed in an Imhoff cone with 500 ml of 4 percent lime slurry. The blend was mixed 10 minutes with air and then rinsed. This treatment was repeated a total of six times to determine how much additional color could be removed by repeated regeneration.

Ammonia regeneration was studied by passing 5 BV of a 4 percent solution of NH_4OH through the resin upflow at 20 BV/hr, followed by the same procedure for rinsing used with lime regeneration. This procedure was repeated three different times on the same resin.

Rejuvenation. During rejuvenation experiments, 15 ml aliquots of used, regenerated resins were placed in 1/2 inch diameter tubes in beds 12 inches deep. Various chemicals such as methanol, 10 percent NaCl, and 1 N HCl were passed downward through the columns at 12 to 16 BV/hr.

DESALINATION IN SINGLE RUNS

The objective of the single runs was to establish near-optimum conditions for operating the time-consuming, difficult cyclic runs.

Cation Exchange

The influent to the cation column was the artificial ditch waste treated by massive lime precipitation and recarbonation to 300 CU and pH 7.6. It was applied at the rate of 20 BV/hr downflow because preliminary runs indicated such a flow rate was near optimum. Duolite C-25D porous cation resin was chosen because its low rinse requirement, high efficiency in regeneration, and good kinetics outweighed the disadvantage of its low capacity as compared to gel type resin. The resin bed, 1 in. ID x 24 in. deep, was a compromise between applicability to prototype conditions and conservation of time and expensive liquor.

During the first test, feed was applied until complete breakthrough of all ions occurred. The column was then backwashed with 10 BV (75 gal water/cu ft resin) of distilled water at a rate of 20 BV/hr which produced a bed expansion of approximately 50 percent. After backwashing, the plenum was dewatered through the middle port and 5 BV of 1 normal HCl (11.4 lb HCl/cu ft resin) was applied upflow at a rate of 20 BV/hr. The acid was immediately followed with 5 BV of distilled water applied upflow at the same rate followed by 10 BV of distilled water rinse applied downflow.

Later in the test program, H_2SO_4 was used instead of HCl and at different flow rates and volumes. Rinse volumes were monitored by conductivity and pH. The breakthrough during the service run was limited to 35 percent.

Anion Exchange

Because the amount of product water from the cation column was so small, feed for the anion column was produced by using a larger cation column, 2 inches ID by 24 inches deep filled with Duolite C-25D, H-form resin. The cation run was stopped when the sodium ion breakthrough reached 35 percent and the specific conductivity had dropped from 6500 to 4000 micromhos. At the pH of the combined effluent, which was about 2, the alkalinity was converted to CO_2, which was stripped by sparging with compressed air until the CO_2 level was approximately 2 mg/l.

In the first run, feed to the anion column was applied downflow at the rate of 20 BV/hr until all anions broke through completely. But after the first run, feed was stopped at a Cl breakthrough of approximately 35 percent. Immediately following the service part of the cycle, the resin was backwashed with 10 BV of distilled water applied at an upflow rate of 16 BV/hr. Then the water was drained from the plenum and typically 5 BV of 1 normal NaOH was applied upflow at 16 BV/hr followed by 5 BV of distilled water at the same rate. Typically upflow rinse was followed by 10 BV of downflow rinse with distilled water at the rate of 16 BV/hr. The column was then ready for a new service run. Nine such preliminary runs were completed with variations of operating parameters to optimize flow rates and volumes of regenerant and rinse.

Regeneration Efficiencies

Regeneration efficiencies were determined in a number of ways. Screening tests were made with several acids and bases and different volumes and rates. Efficiencies were determined by measuring ions sorbed by resins and checked by measuring ions eluted by the regenerant.

The rinse requirement was determined by monitoring conductivity and pH. The volume of rinse was deemed sufficient when the conductivity of the rinse effluent was approximately equal to the conductivity of the feed.

DESALINATION IN CYCLIC RUNS

Feed to the cation column was artificial ditch waste pretreated by massive lime precipitation and two-stage recarbonation to a residual color of 300 CU. The feed was pumped downward through a 1 in. ID column containing 24 inches of Duolite C-25D resin at a flow rate of 20 BV/hr because preliminary tests showed such a flow rate was near optimum. Flow was continued to a 35 percent breakthrough of the sodium ion.

The resin was regenerated with 1.3 BV of 3 percent technical grade H_2SO_4 applied at the rate of 16 BV/hr in upward flow. Regeneration was immediately followed by 3 BV of distilled water at the same rate.

The cation product water was stored in a barrel, degasified by air sparging to a residual concentration of 2 mg/l CO_2. This well-mixed product was pumped to the anion column (also 1 in. ID filled to a depth of 24 inches with Duolite A-6 resin) at the rate of 20 BV/hr downflow. The run was continued to a 35 percent breakthrough of the chloride ion. The resin was regenerated with 1.3 BV of 3 percent technical grade NaOH applied upflow at the rate of 16 BV/hr. The caustic was followed with 3 BV of distilled water at the same flow rate.

The flow rates, volumes, and concentrations of regenerants and volumes of rinse were nearly optimum values determined from the preliminary tests. With only a minimum of compromise, the operating parameters could therefore be made the same for both resins. This was done in the interests of ease of operation.

One series of runs was made at a temperature of 60°C to simulate the temperatures to be found under actual mill conditions. The feed to the columns was preheated in a Blue M water bath before introduction into the environmental cabinet which contained all of the ion exchange equipment held under a temperature of 60°C ± 1°.

REMOVAL OF RESIDUAL COLOR

The high rate of flow, starvation regeneration, and the limited bed depth of 24 inches permitted an average leakage of about 80 color units. Several procedures were tried for the removal of residual color after desalination by ion exchange.

Decoloring methods tried unsuccessfully on desalinated water included virgin Duolite S-30 in OH form, Filtrasorb 400 carbon, Carbo-Dur carbon, Duolite A-7 resin ground to 100 x 200 mesh in virgin OH form, and A-6 in 40 to 80 mesh virgin base form. The various sorbents were tested at a downflow rate of 20 BV/hr in 1 inch ID by 24 inch deep beds.

Finally, second stage demineralization was tried for the removal of residual color with used C-25D cation resin and used A-6 anion resin. The cation resin was conditioned with 2 BV of 3 percent H_2SO_4 and the anion resin was conditioned with 2 BV of 3 percent NaOH. The slightly colored (80 CU) effluent from the first stage was put through the cation column at a downflow rate of 20 BV/hr, the effluent was collected, stripped of residual CO_2 by air sparging, and then put through the anion column downflow at a rate of 20 BV/hr. Samples were collected at intervals of 5, 10, 20, 40, 80, 120, etc. BV for color monitoring.

LIFE TESTS

Column Operations

All resins and sorbents were confined in beds 1 inch ID by 2 inches deep, a volume of 28 ml. The resins tested included the following strong acid resins: C-25D, Amberlite 200, HCR-W, IR-120+; the following weak acid resins: IRC-50, and IRC-84; the following strong base resins: Dowex 11 and IRA-402; the following weak base resins: A-6, A-7, IRA-68, and IRA-93; and the following synthetic sorbents: S-37, S-30, ES-33, and XAD-8.

Feed. All columns were operated simultaneously on the same cyclic times. Feed to the cation resins was artificial ditch waste pretreated to 300 CU and pH 7.6. Feed to the anion column was a well-mixed cation effluent at pH 2 from which the CO_2 was removed by air sparging. The cation column was operated until the sodium breakthrough at the end of the run was 35 percent. The average sodium leakage was 2.2 percent or about 0.28 me/l.

Regenerants. Regenerant for the cation column was 3 percent technical grade hydrochloric acid and, for the anion and sorbent resins, 3 percent technical grade NaOH.

Cyclic regime. The flow rate was 8.0 ml per minute which was equivalent to 17 BV/hr. The regeneration time was 5 minutes, and the service time was 140 minutes. All the flows were applied upward to prevent plugging the column, but the flow rates were so low no expansion of the resin bed nor movement of resin particles occurred. This scheme allowed particles in the feed to be washed right through the resin column. The effluent was only monitored for the determination of flow rate which was kept well within ± 5 percent.

Inspections

An inspection consisted of visual examination using a 30 power stereoscopic microscope with both direct and reflected light and for the determination of exchange capacity. At the beginning and the end of the life tests the volume and weight of the resin were determined under standard conditions.

Preparation. Resins were prepared for inspection by conditioning with 5 BV of 1 N reagent grade NaOH (for anion resins) or HCl (for cation resins) downflow at 8 ml/min. They were rinsed until the effluent pH was approximately neutral.

Exchange capacity. Exchange capacity was determined by exhausting the resin at the rate of 8 ml/min in downflow. Feed for strong acid resins was 0.5 N reagent grade NaCl to a neutral effluent, which required approximately 800 ml of liquor. The exchange capacity of strong base resins was determined by feeding 5 percent reagent grade NaCl to a neutral effluent which required approximately 650 ml of liquor. The feed for weak base and sorbent resins was 810 ml of 0.135 N reagent grade HCl, and the feed for weak acid resins was 1250 ml of 0.10 normal reagent grade NaOH. Effluents were collected, and titrated to neutrality with 0.5 N reagent grade NaOH or HCl. These procedures varied somewhat from manufacturers' recommendations, but they were found to give the same results and possess the advantage of ease and quickness of operation.

Sorptive capacity was tested by thoroughly regenerating the resin with N/12 NaOH until the effluent was colorless. It was rinsed with distilled water to neutral pH. Then 30 BV of a "standard" artificial ditch waste acidified to pH 2.2 was passed upward through the column at 12 BV/hr.

The exhausted resins were returned to the life cycling apparatus which was set to regenerate them as the first step in the cycle.

Frequency. Inspections were made of the resins periodically as follows: virgin resin, after 20 hours of service, then at intervals increasing up to 200 hours.

CHEMICAL ANALYSES

The procedures used for chemical analyses are described in Table 11.

TABLE 11

PROCEDURES FOR CHEMICAL ANALYSES

Determination	Method	Reference
Cations		
Sodium	Flame spectrophotometry at 589.3 mμ. Dilution to 10 me/l max.	SM[a] p. 317
Potassium	Flame spectrophotometry at 768 mμ.	SM p. 283
Calcium	Titrimetric with EDTA. Triethanolamine added. Hydroxy-naphthol blue indicator.	SM p. 84
Magnesium	Titrimetric (hardness) with EDTA. Triethanolamine added, Eriochrome black T + methyl red indicator. Ca subtracted from hardness.	SM p. 179
Anions		
Alkalinity	Titrimetric (total alkalinity) with N/50 H_2SO_4 to inflection point at pH 4.5±	SM p. 52
Chloride	Titrimetric with $Hg(NO_3)_2$. Diphenyl-carbazone, xylene cyanol FF indicator.	SM p. 97
Sulfate	Turbidimetric. Precipitation with $BaCl_2$ after color removed with 10 g/100 ml powdered activated carbon.	SM p. 334

Table continued

(Table 10 continued)

Determination	Method	Reference
	Also: Ignite 20 minutes at 600° C for color removal. Dilut decationize and add dioxane. 0.0141 N $BaCL_2$ titrant. Thorine indicator.	USGS #1454, pp 270-271.
Sulfide	Titrimetric with $Na_2S_2O_3$. Sulfide evolved as gas and collected in zinc acetate solution.	SM p. 552
Nitrate	Phenoldisulfonic acid. λ = 410 mμ. Interfering color removed with 0.5 g powdered activated carbon and 1 ml $Al(OH)_3$ cream/50 ml.	SM p. 234
Other Chemicals		
Chlorine		
Total	Iodometric. 0.01N $Na_2S_2O_3$ standardized daily. Starch indicator.	SM p. 110
Total	Amperometric at pH 4. Phenylarsene oxide	SM p. 112
Free	Amperometric at pH 7. Otherwise as noted above.	SM p. 115
pH	Glass electrode. Sargent Model DR or Orion Model 404 pH meter.	
Total organic carbon (TOC)	Batch tests: Beckman Carbonaceous Analyzer. N_2 sparging at pH 2. Column tests: Early column tests: titration of inorganic carbonates. Late column tests: Beckman M-915 total organic carbon analyzer.	

Table continued

(Table 10 continued)

Determination	Method	Reference
Biochemical oxygen demand (BOD)	Bottle dilution method using aerated Clark Fork River water without added seed, buffers, or nutrients.	SM p. 489
Chemical oxygen demand (COD)	Dichromate method.	SM p. 495
Conductivity	Lectro Mho-meter.	Manual #9-056-199-00 Labline Insts., Inc.
Physical Tests		
Color (CU)	Hitachi Perkin-Elmer M-139 at λ = 422.2 mμ. Filtration with 0.45μ Millipore filter and adjustment to pH 7.6. 500 mg/l Pt (in chloroplatinate form) = 500 CU.	SM p. 392
Color analysis	Filtration with 0.45μ Millipore. 10-point tristimulus values for dominant wave length, hue, luminance, and purity.	SM p. 392
Suspended solids (SS)	Vacuum filtration with Whatman #30 paper in 9 cm Buchner funnel.	SM p. 290
Total dissolved (TDS)	Evaporation of SS filtrate over hot water and drying at 103°C.	

[a] Standard Methods (1971)

SECTION VII
RESULTS AND DISCUSSION

EXPLORATORY TESTS

Several kinds of tests and experiments were performed to ensure accuracy in measurements and to determine the effect of several test variables. They included tests for: sorption of color bodies on the walls of spectrophotometer cells, effect of temperature on sorption, variation of color with pH, means for the measurement of true color of turbid suspensions, effect of time of storage, calibrations, and determining the most reliable methods for chemical analysis of these highly colored solutions.

Isotherms and color sorbency tests were run on a wide variety of sorbents and anion exchange resins. The results from these tests were the basis for selecting resins to be investigated in the more time-consuming column operations.

Miscellaneous Tests

Spectrophotometer cells. Adherence of organic material to the walls of spectrophotometer cells has been known to cause spurious readings. But a series of tests using bleach wastes indicated organic material did not adhere to the cell walls enough to effect results appreciably.

Color measurement. Several means were tried for removing the turbidity which interferred with color determinations including: filtration through Whatman No. 30 filter paper and through 0.45 μ, 0.2 μ and 0.8 μ Millipore filters, and centrifugation at 2000 rpm and 17,000 rpm for 20 minutes each.

The results were not greatly different. For the small volume of samples required, filtration through a 0.45 μ Millipore filter held in a 25 mm Swinnex filter holder was the quickest and the most satisfactory treatment for routine work. The Swinnex filter holder was attached to a Millipore Sanitarian's syringe modified to filter by pressure instead of vacuum.

A typical calibration curve is shown in Figure 6. Color measured at 422.2 mμ is practically the same as color measured at 420 mμ because the spectrum is flat in this region. The odd wave length was used because it is one of the wave lengths specified in obtaining tristimulus values.

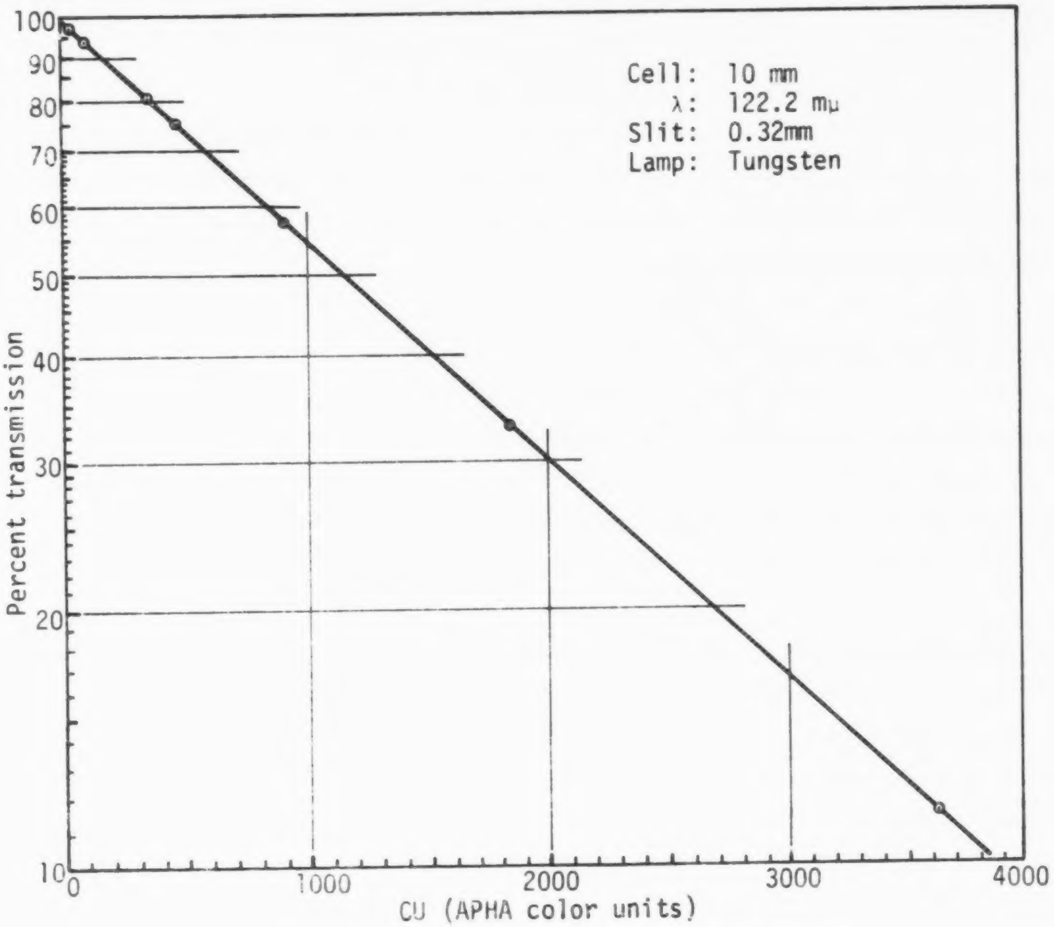

FIGURE 6. CALIBRATION OF SPECTROPHOTOMETER

Total organic carbon. During the first two years of the investigation, the carbonaceous analyzer was often inoperative. A new Beckman Model 915 Total Carbon Analyzer was obtained during the last stages of this investigation, so a few reliable results of total organic carbon were obtained. Unfortunately, most of the value of total organic carbon measurements pertained to the preliminary phases of the work.

The National Council for Stream Improvement, Inc. (1962) found TOC was directly proportional to color in 20 different caustic stage effluents. In the tests reported herein, proportionality did not occur between color and organic carbon during sorption runs by carbon and resins.

Mixing and sorption. The rate of sorption in batch tests is strongly influenced by mixing due to the renewal of the average concentration at the liquid-solid interfaces. Tests to establish the effect of agitation rate showed an increase of sorption with increasing agitation up to 100 cpm. Above this value there was no increase of sorption with an increase in agitation. Consequently, all batch sorption tests were made at an agitation rate of 112 cpm.

Storage. The problem of preventing changes in stored wastes was thought to be a serious difficulty. Dugal (1969) concentrated and preserved wastes by vacuum distillation followed by freeze-drying to a powder.

Samples of our wastes were sent to Dugal for trial freeze-drying. The caustic extract could not be concentrated by vacuum distillation because freezing made the product gummy and sublimation to a powder did not occur. Freeze-drying without previous concentration by vacuum distillation was successful, but this was too time consuming for the preservation of large quantities.

Freezing might be thought to preserve the wastes almost unchanged, but Abrams (1969) and others found precipitates often form as the temperature is reduced. The precipitates do not redissolve as the temperature is raised. An exploratory check of this observation was made with some filtered black liquor extract. After thawing the frozen liquor, large particles were seen and the color increased 7 percent. Refiltering had no affect upon the color.

Cold storage did not appear to be particularly advantageous. Color in chlorine stage wastes decreased about 4 percent in a month. Color in caustic waste declined from 4 to 20 percent in about the same period. Color in ditch waste declined from 30 to 40 percent, and color in hypochlorite and chlorine dioxide liquids were drastically reduced on a percentage basis. However, the latter two liquors were not highly colored at the time of collection (approximately 40 CU) so a large percentile change was comparatively insignificant.

At room temperature, color in the chlorine waste decreased only 10 percent in 70 days and color in the caustic waste increased only 7 percent. Thereafter, wastes were stored at room temperature.

In this exploratory phase of the program, some alteration of the waste was tolerable. If it were known that only the amount, and not the character, of the color bodies were changed, alteration could have been tolerated throughout all the investigations. Insofar as has been determined, there seems to be no apparent change in the distribution of molecular sizes as determined by gel permeation chromatography using a Sephadex column. But such tests are relatively crude and inconclusive.

Temperature and sorption. In general, the rate of sorption increases with an increase in temperature. Several tests indicated the increase in sorption rate between 15°C and 20°C was scarcely detectable. Above 20°C the rate of sorption increased markedly. Hence, sorption tests were run between 17°C and 20°C. Closer temperature control was unnecessary.

Isotherms in Batch Tests

Twelve isotherms were run before the program of establishing isotherms for each waste and each resin was modified to the determination of 4-hour color sorbency tests. The time required to reach apparent equilibrium varied greatly but was usually more than a week. Moreover, true equilibrium was elusive because at the end of a week color was often sorbed so slowly that the determination of whether true equilibrium was achieved itself required several days. As the capacities of the shaking machines were limited, the use of isotherms for selecting the best resins for column tests became impractical.

While isotherms are useful for selecting carbon they are less so for selecting resins. Each point on an isotherm represents equilibrium. Because even highly colored wastes contain relatively small amounts of organic material and because carbon has a high equilibrium capacity for organic material (up to 25 percent of its own weight) the lower layers in a deep carbon column would be expected to approach equilibrium in an upflow reactor. But resins, on the other hand, should be regenerated frequently to prevent irreversible sorption or poisoning. Since resins would not be subject to equilibrium in service, isotherms for resins and carbons cannot be compared. To be valid, the pilot plant operation must simulate the prototype, and the costs of equipment and operation must be measured against the efficacy of treatment. Hence, it is proper to compare carbons by means of isotherms and to compare esins by means of short sorbency tests, but it is unreasonable to use either of these methods to compare carbon with resins. Therefore, the modification of original plans to obtain isotherms for all sorbents and wastes detracted little from the program.

Both Langmuir and Freundlich isotherms were plotted. The Langmuir isotherm is considered to be rational and the Freundlich isotherm empirical. Neither, however, explains the phenomenon of sorption and as both are only a means for fitting data, the choice is largely one of preference. Because the Freundlich isotherm invariably fit the data better, it was the isotherm of choice. The more complex Brunauer-Emmett-Teller isotherm, which is adapted to multiple layers of sorbed molecules, was not considered.

These data are not invariably good. Some points lie at considerable distance from the best straight line. Plots of time versus sorbency indicated no sorbent reached full equilibrium at all doses over the time periods tested, namely 120 to 196 hours.

All carbons abraded severely creating particles fine enough to pass through Whatman No. 31 filter paper. Some resins abraded too, although not as much as carbon. Probably tumbling at short, intermittent periods would reduce abrasion and would seem to be superior to constant, violent shaking.

Resins. Isotherms for caustic extract and ditch waste are shown in Figures 7 to 13 for the following types of resins: strong base gel, weak base phenolic exchanger, weak base epoxy-amine, and two weakly basic phenolic sorbents.

None of the resins tested were effective on caustic waste, but all were effective on ditch waste. The sorption of color from ditch waste must have included the sorption of some components of caustic extract color, because total color sorption was considerably greater than the color contribution of chlorine waste. This synergistic effect was observed many times.

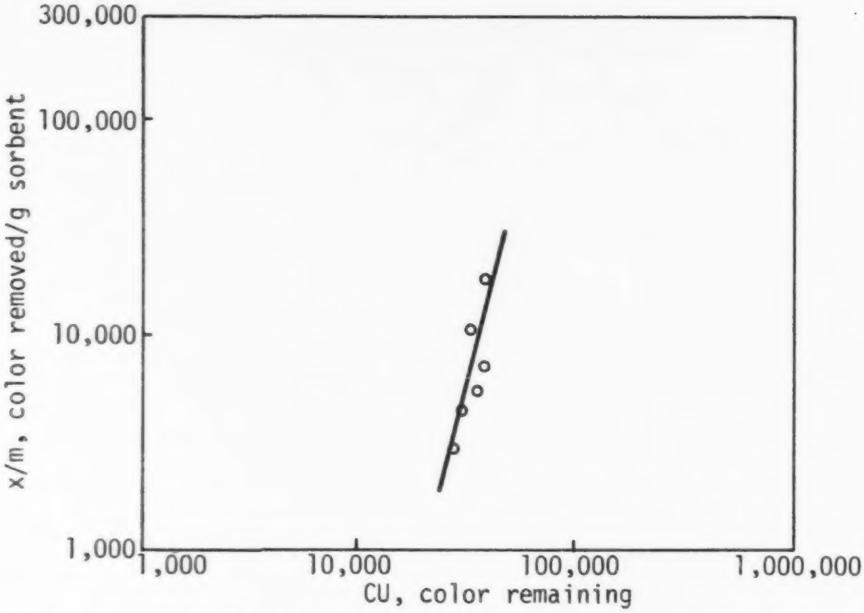

FIGURE 7. FREUNDLICH ISOTHERM FOR DOWEX 11 AND CAUSTIC

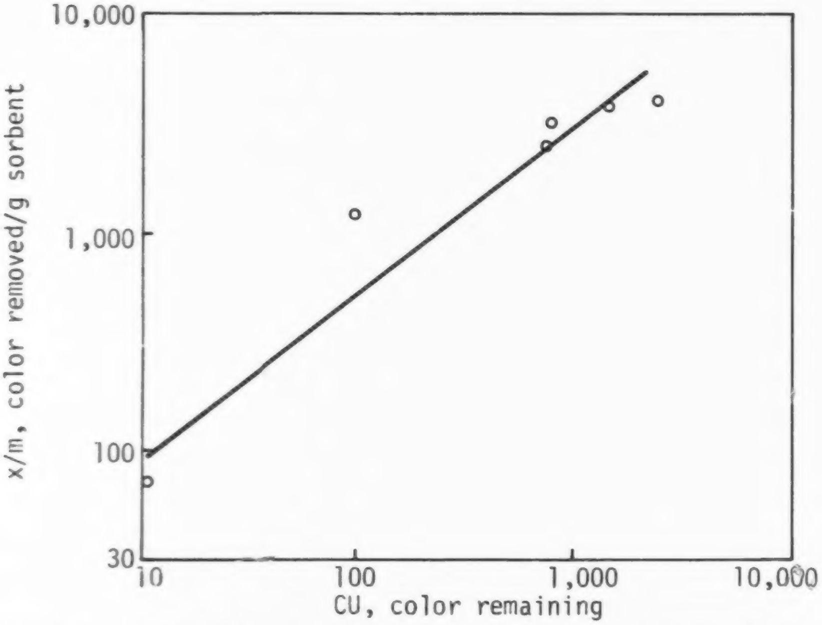

FIGURE 8. FREUNDLICH ISOTHERM FOR DOWEX 11 AND DITCH WASTE

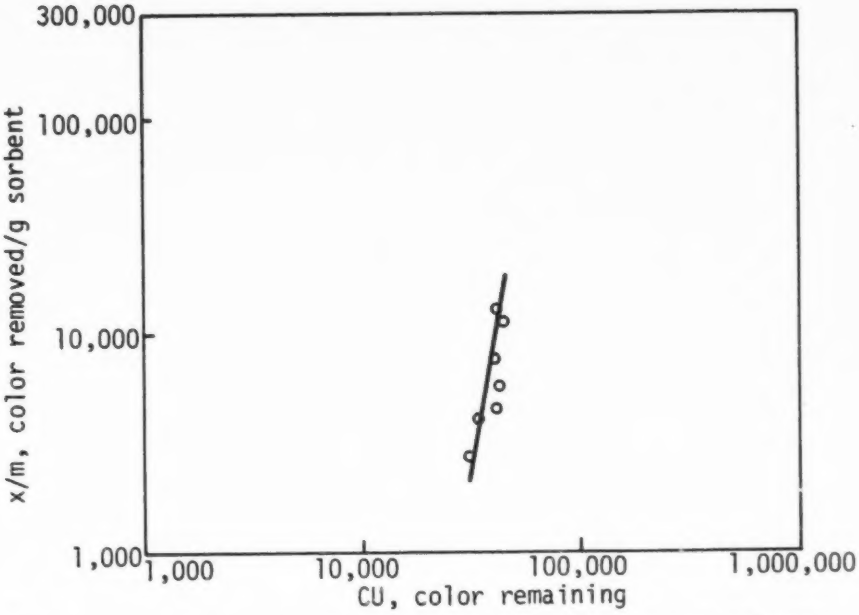

FIGURE 9. FREUNDLICH ISOTHERM FOR DUOLITE A-7 AND CAUSTIC

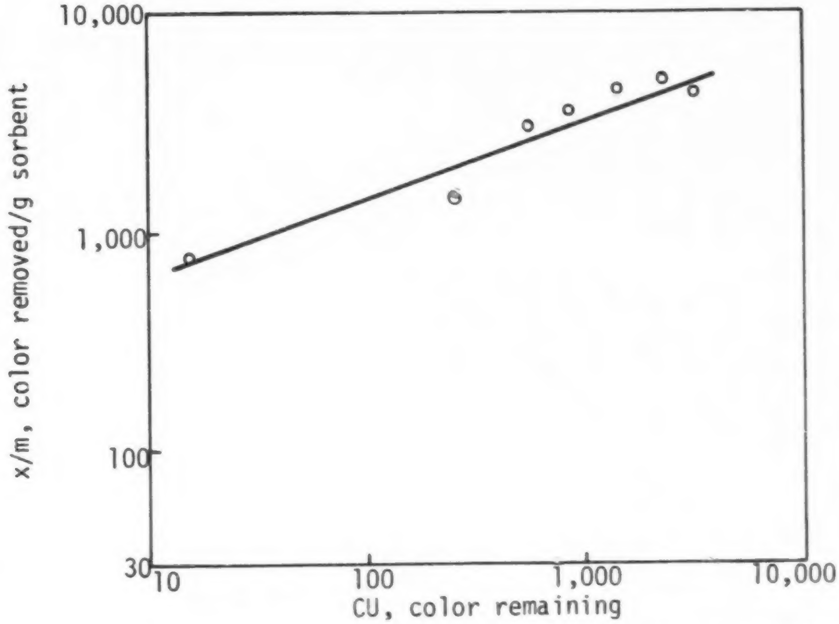

FIGURE 10. FREUNDLICH ISOTHERM FOR DUOLITE A-7 AND DITCH WASTE

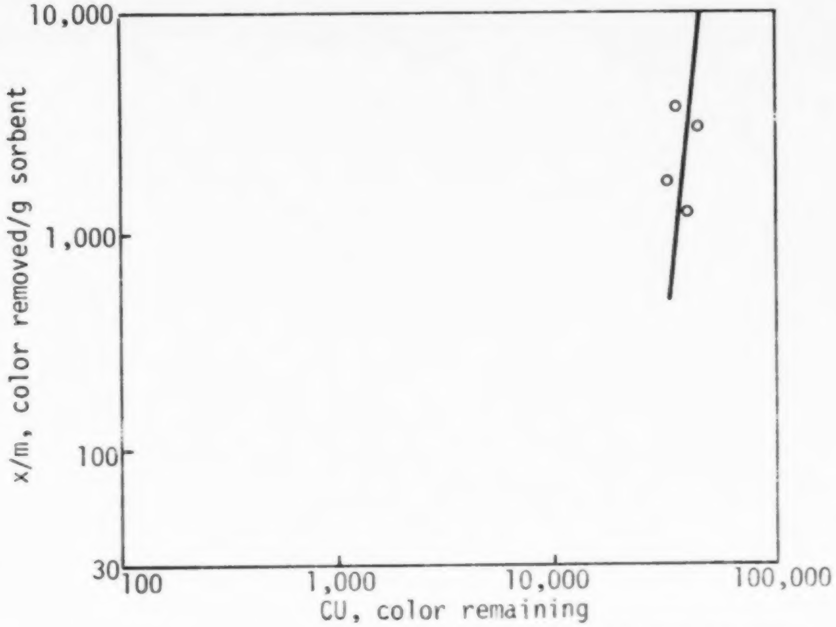

FIGURE 11. FREUNDLICH ISOTHERM FOR DUOLITE A-57 AND CAUSTIC

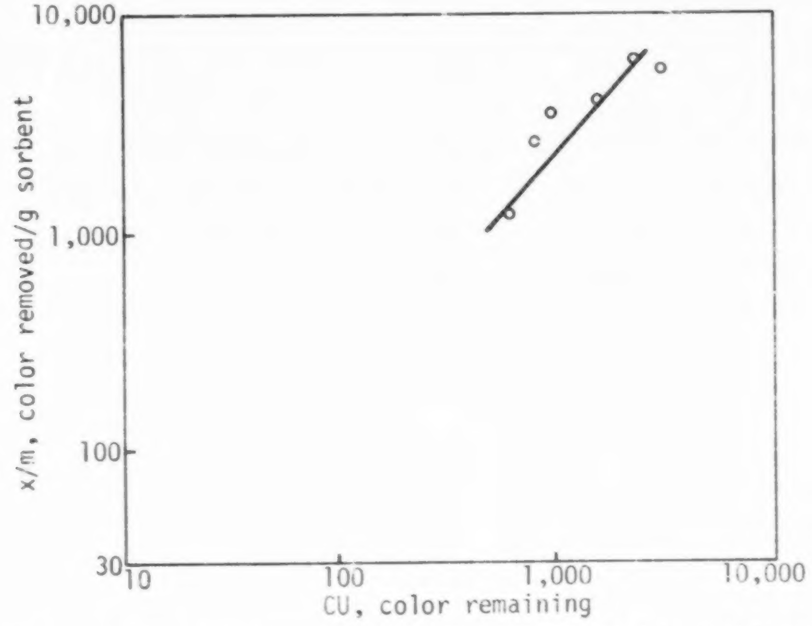

FIGURE 12. FREUNDLICH ISOTHERM FOR DUOLITE ES-33 AND DITCH WASTE

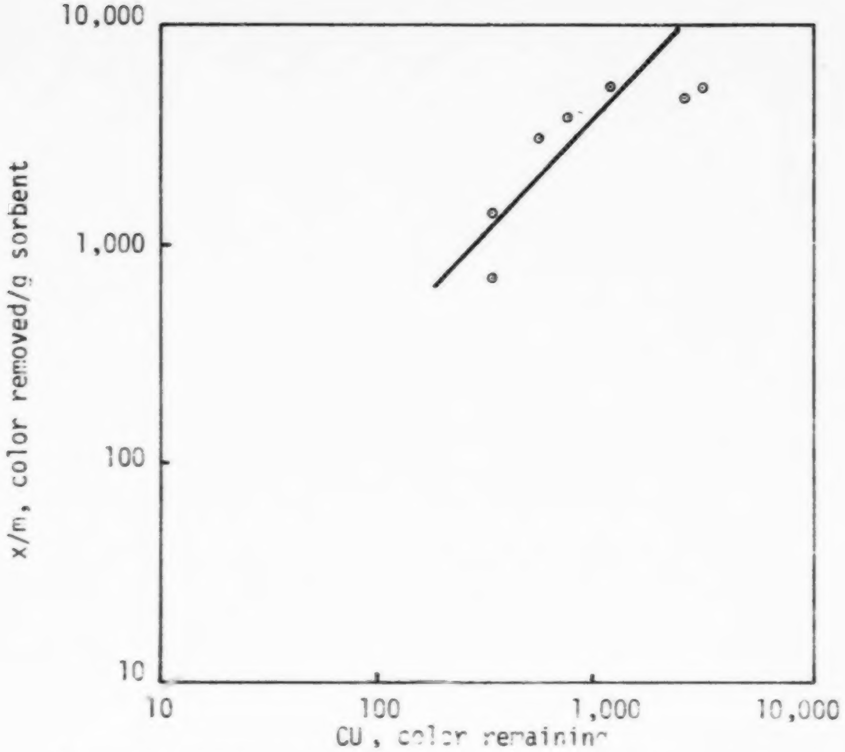

FIGURE 13. FREUNDLICH ISOTHERM FOR DUOLITE S-37 AND DITCH WASTE

The resins listed in order of merit for sorbing color from ditch waste are: Duolite A-7, Dowex 11, Duolite S-37, and Duolite ES-33. Duolite A-7 was much better than all the others. Abrams (1969) found phenolic matrices to be superior to polystyrene and weak base to be better than strong base functional groups for sorption of some kinds of organic materials. The results obtained herein confirm this viewpoint.

Carbon. Isotherms of sorption of color by carbon from caustic extract, ditch waste, and chlorine waste are shown in Figures 14 to 18. All carbons tested were effective on all wastes tested.

Filtrasorb 300 appeared to be slightly superior to Nuchar VWL in the sorption of color from caustic extract and somewhat inferior for ditch waste, but the difference was not great. Both carbons performed

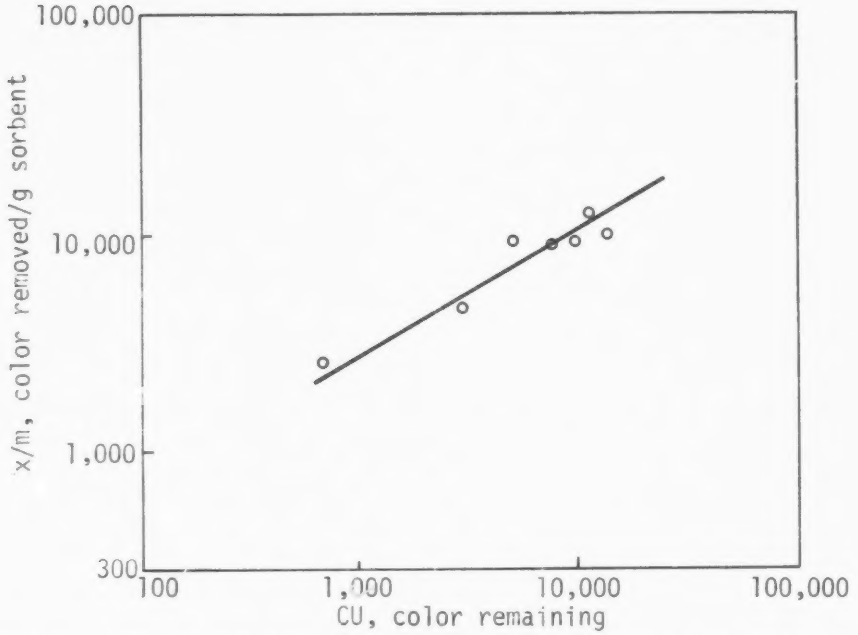

FIGURE 14. FREUNDLICH ISOTHERM FOR FILTRASORB 300 AND CAUSTIC WASTE

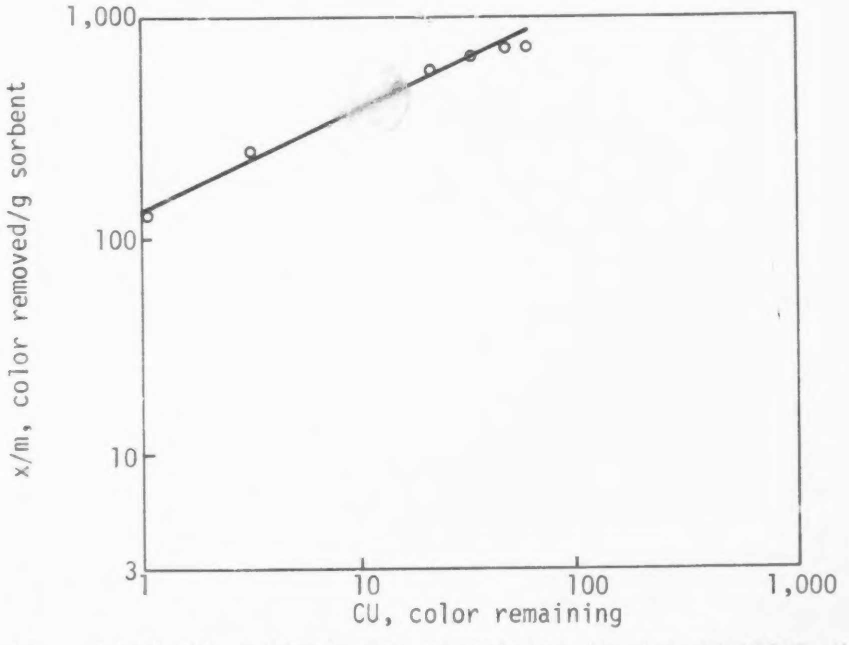

FIGURE 15. FREUNDLICH ISOTHERM FOR FILTRASORB 300 AND CHLORINE WASTE

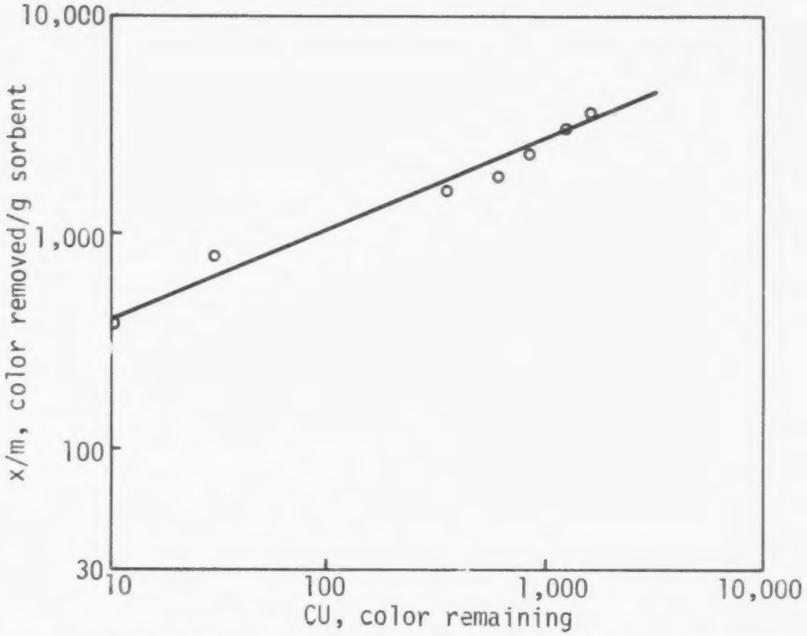

FIGURE 16. FREUNDLICH ISOTHERM FOR FILTRASORB 300 AND DITCH WASTE

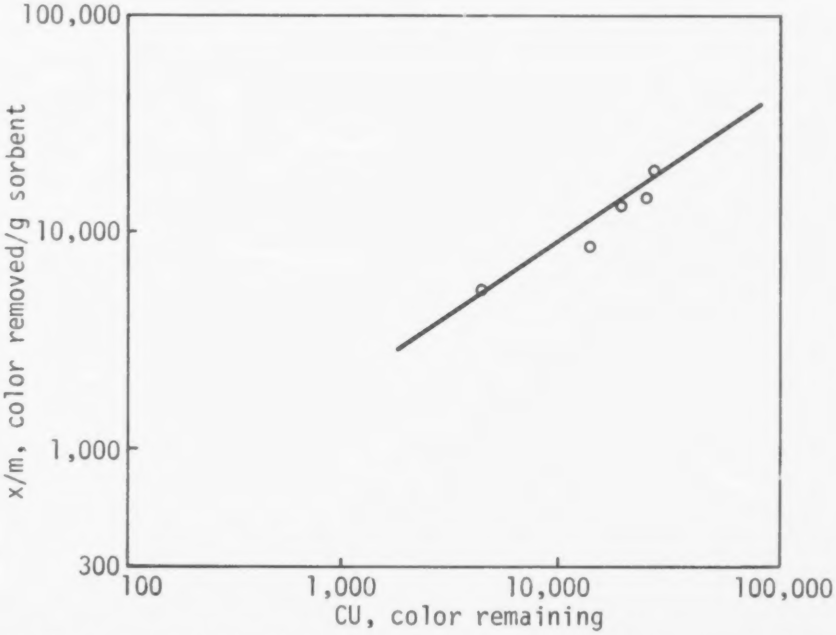

FIGURE 17. FREUNDLICH ISOTHERM FOR NUCHAR WVL AND CAUSTIC WASTE

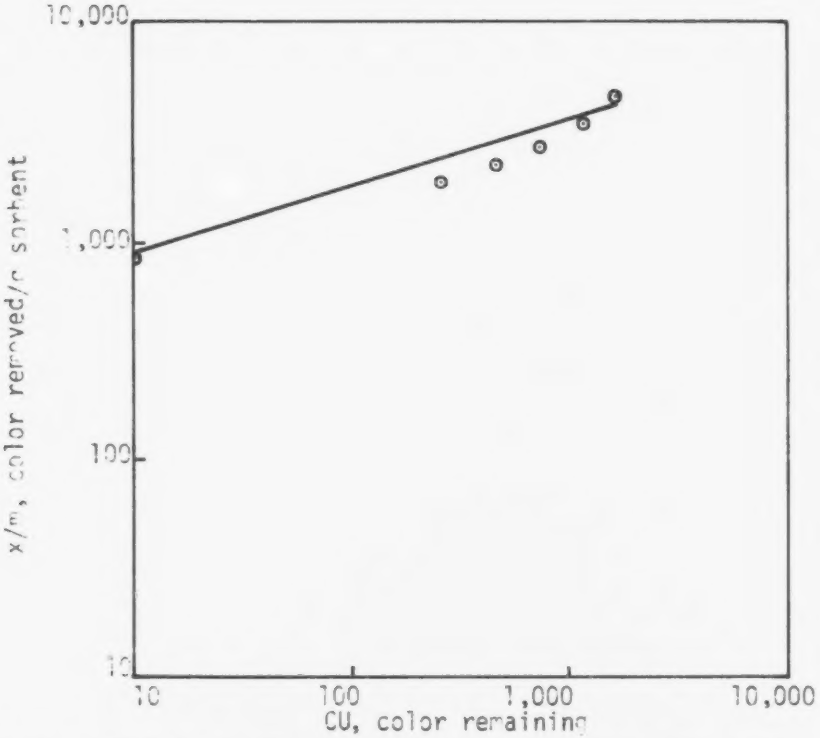

FIGURE 18. FREUNDLICH ISOTHERM FOR NUCHAR WVL AND DITCH WASTE

well. In contrast to resins, carbon sorbed color from caustic extract waste much better than from ditch waste. Sorption from ditch waste was better than from chlorine wastes.

Color Sorbency in Batch Tests

Representative curves of color sorbency over a four-hour period are shown for several sorbents in Figures 19 to 25. The conditions for these and all other color sorbency tests are given in Table 12.

It must be noted that these curves cannot be taken at face value for many reasons, among them:

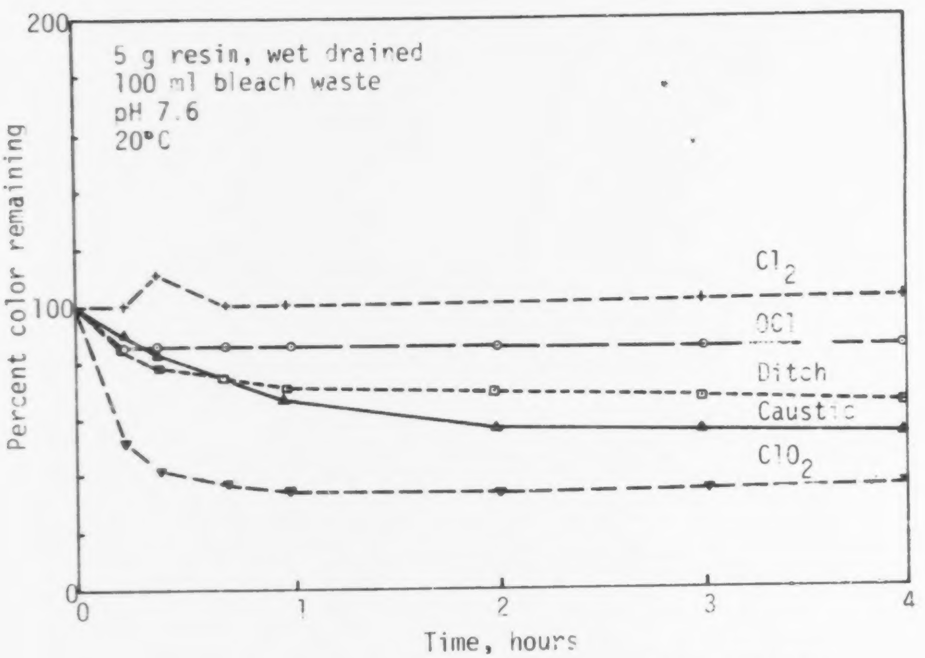

FIGURE 19. AMBERLITE IRA-68 RESIN, COLOR SORPTION

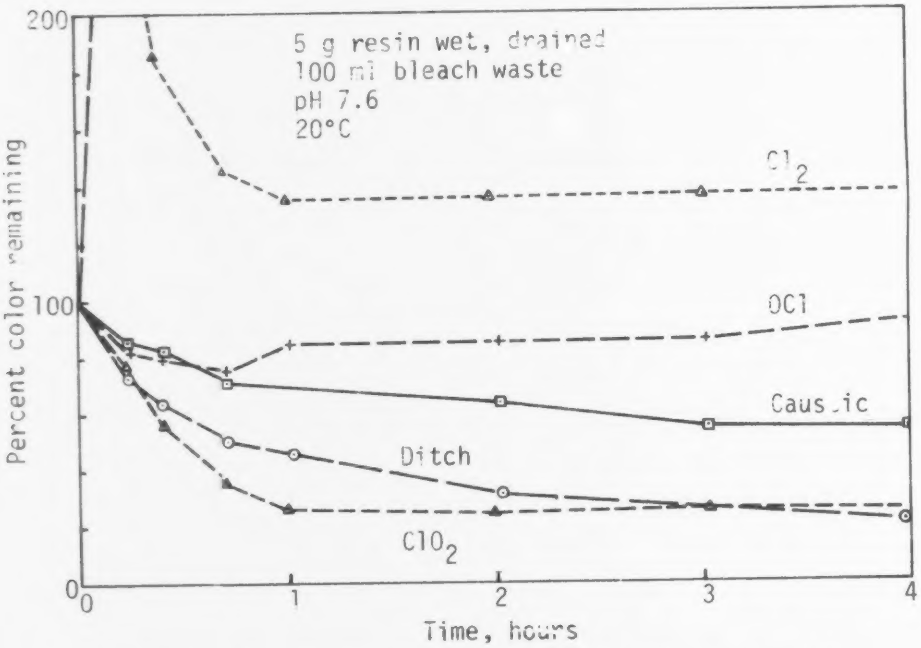

FIGURE 20. AMBERLITE IRA-93 RESIN, COLOR SORPTION

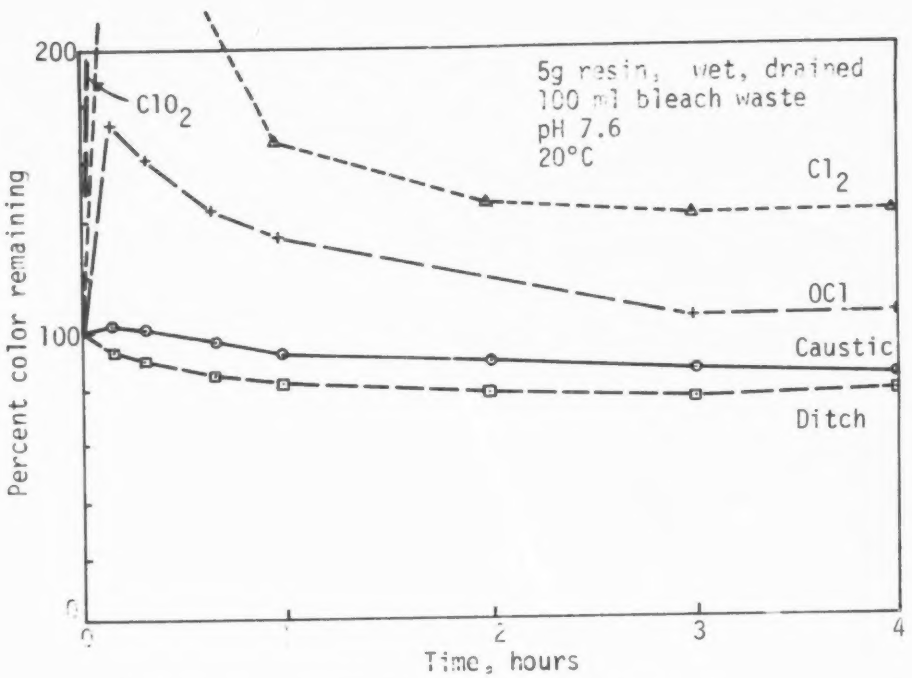

FIGURE 21. DOWEX 11 RESIN, COLOR SORPTION

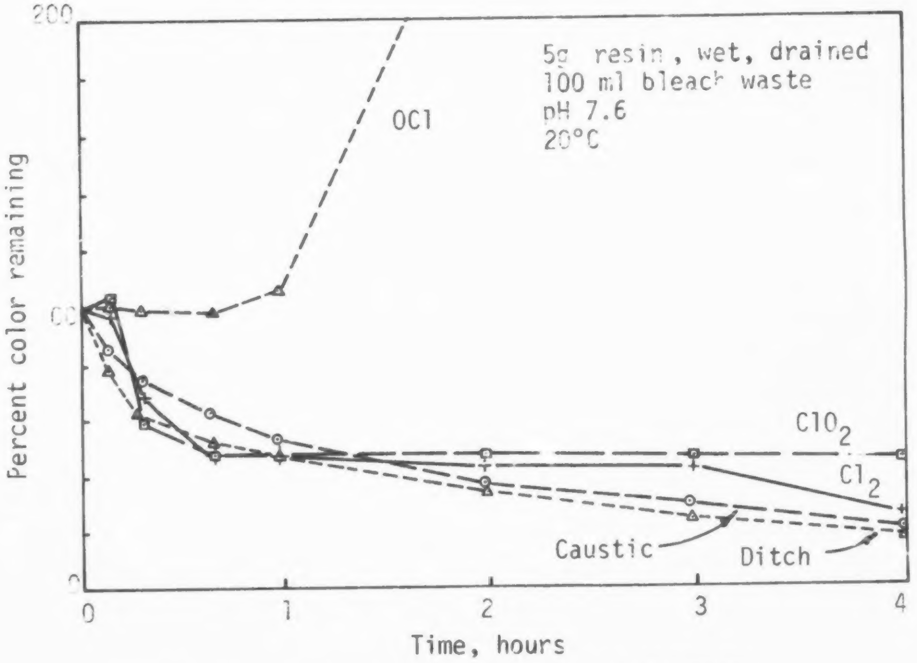

FIGURE 22. DUOLITE A-6 RESIN, COLOR SORPTION

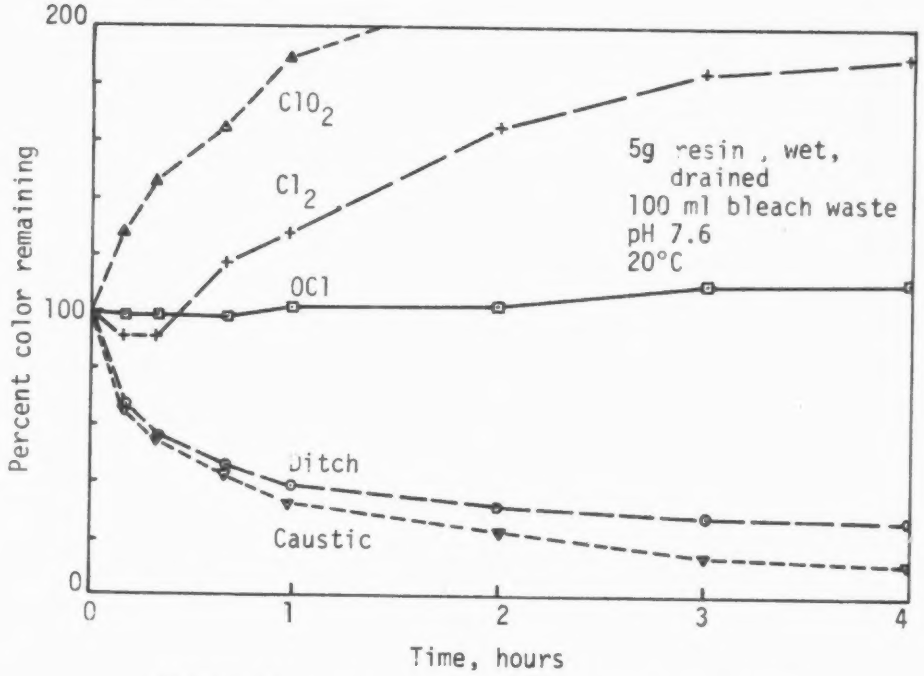

FIGURE 23. DUOLITE A-7 RESIN, COLOR SORPTION

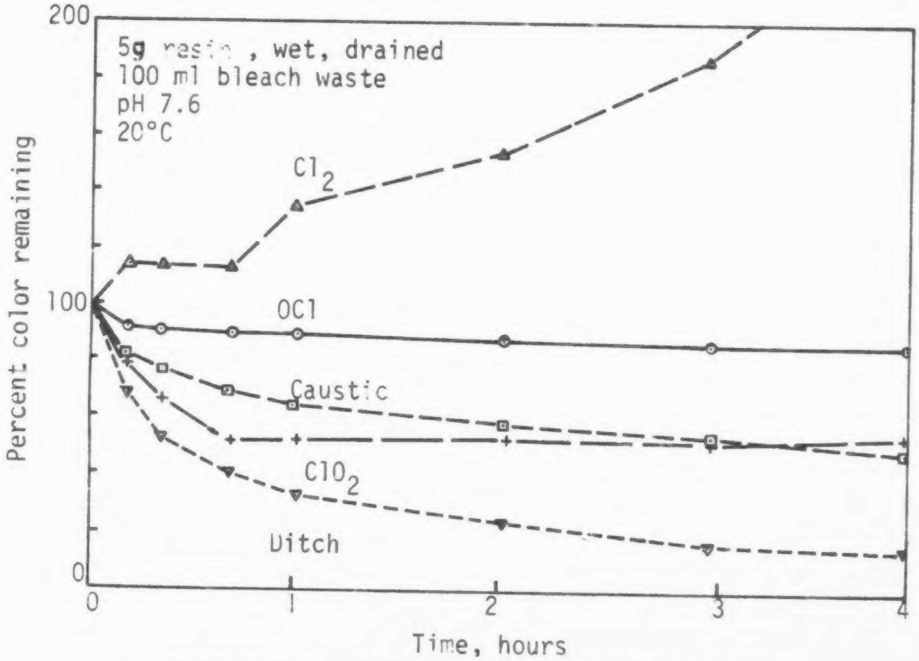

FIGURE 24. DUOLITE S-37 RESIN, COLOR SORPTION

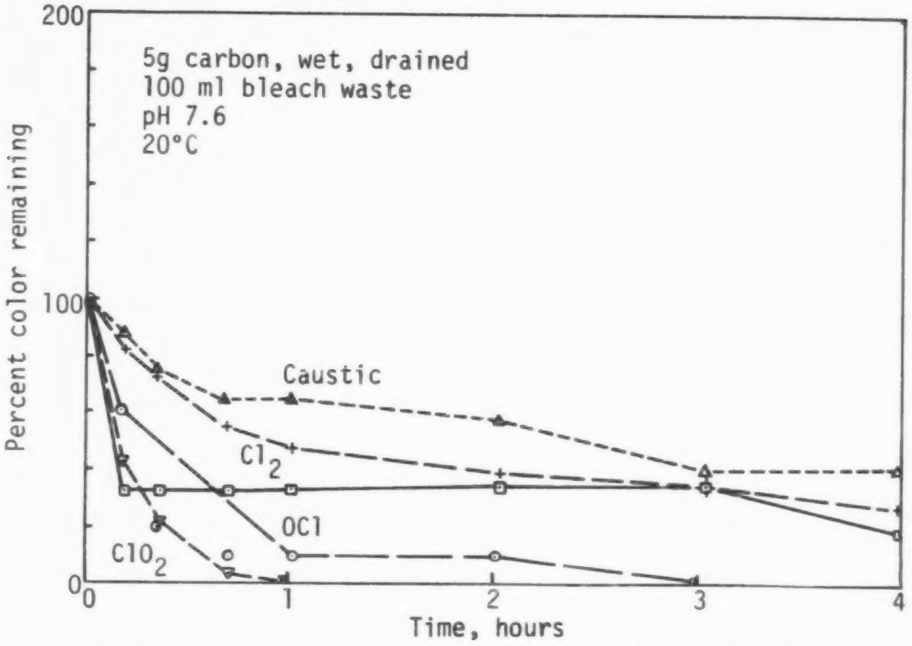

FIGURE 25. FILTRASORB 300 CARBON, COLOR SORPTION

TABLE 12

SUMMARY OF DATA FOR COLOR SORBENCY

Type Bleach Waste	APHA Color Units		
	Raw	End	Red. %,[a]
ANION RESINS			
Amberlite IRA-68			
Cl_2	570	570	0
Caustic	25400	13400	47
Hypo	254	214	16
ClO_2	168	54	68
Ditch	4860	3010	48
Amberlite IRA-93			
Cl_2	57	80	-40,[a]
Caustic	25900	14000	46

(Table 12 continued)

Hypo	254	219	14
ClO_2	170	39	77
Ditch	4860	895	82
Dowex 11			
Cl_2	57	715	-1150
Caustic	26900	22400	17
Hypo	270	277	-3
ClO_2	155	360	-132
Ditch	4710	3550	25
Dowex WGR			
Cl_2	57	149	-161
Caustic	26400	25400	4
Hypo	258	245	5
ClO_2	18	7	61
Ditch	4860	4450	7
Duolite A-6			
Cl_2	130	35	73
Caustic	25400	2950	-88
Hypo	105	230	-119
ClO_2	140	60	57
Ditch	4590	840	82
Duolite A-7			
Cl_2	57	485	-751
Caustic	26900	3300	88
Hypo	270	296	-10
ClO_2	160	392	-145
Ditch	4710	1260	33
Duolite A-57			
Cl_2	57	352	-518
Caustic	26300	24000	9
Hypo	269	261	7
ClO_2	167	360	-116
Ditch	4860	3730	23

(Table 12 continued)

CATION RESINS			
Dowex HCR-W			
Cl_2	140	970	-593
Caustic	16300	16600	-2
Hypo	130	970	-646
ClO_2	230	1210	-424
Ditch	4500	5390	-20
Duolite C-25D			
Cl_2	140	230	-64
Caustic	16300	16600	-2
Hypo	130	100	23
ClO_2	230	205	11
Ditch	4500	4590	-2
SORBENTS			
Amberlite XAD-2			
Cl_2	57	123	-116
Caustic	25300	20000	21
Hypo	253	269	-6
ClO_2	163	102	37
Ditch	4860	3290	35
Duolite S-30			
Cl_2	135	120	11
Caustic	18000	14000	22
Hypo	55	170	-209
ClO_2	145	145	0
Ditch	4590	2350	49
Duolite ES-33			
Cl_2	57	59	-4
Caustic	26300	18000	32
Hypo	219	222	-1
ClO_2	168	168	0
Ditch	4710	1620	66
Duolite S-37			
Cl_2	58	115	-98
Caustic	26300	12950	51

(Table 12 continued)

Hypo	218	190	13
ClO_2	168	95	43
Ditch	4710	650	86
Filtrasorb 100			
Cl_2	50	5	90
Caustic	18400	13000	29
Hypo	50	20	60
ClO_2	125	10	93
Ditch	4230	2540	40
Filtrasorb 200			
Cl_2	50	3	94
Caustic	18400	12000	35
Hypo	50	3	94
ClO_2	130	2	98
Ditch	4230	1990	53
Filtrasorb 300			
Cl_2	30	0	100
Caustic	18000	9990	44
Hypo	50	0	100
ClO_2	120	1	99
Ditch	4230	1450	67
Filtrasorb 400			
Cl_2	30	1	97
Caustic	18000	5850	67
Hypo	50	0	100
ClO_2	120	0	100
Ditch	4230	1000	77
Nuchar WVG			
Cl_2	105	1	99
Caustic	18000	7000	61
Hypo	55	5	91
ClO_2	170	0	100
Ditch	4360	1400	78

(Table 12 continued)

Nuchar WVL			
Cl_2	105	0	100
Caustic	18000	6500	64
Hypo	55	0	100
ClO_2	170	0	100
Ditch	4360	1530	65
Nuchar WVW			
Cl_2	105	0	100
Caustic	18000	8700	52
Hypo	55	5	91
ClO_2	170	0	100
Ditch	4360	1470	66

[a] Negative indicates increase not reduction

(1) All the batch tests were run at pH 7.6 whereas in a prototype situation the pH might be very different and the effectiveness of the sorbent likewise very different. This would be true especially for wastes to be demineralized.

(2) Some of the wastes were lightly colored so percentile reductions are of different significance for different wastes.

(3) In some cases the color actually increased, probably indicating oxidation of the sorbent.

(4) The effect of multiple exhaustion and regeneration cycles was missing and hence utilizing these curves to draw conclusive comparisons between strong and weak electrolyte resins would be premature. Some generalizations, however, are apparent. When there was little or no color sorption or desorption within a four-hour period, the sorbent was obviously ineffective. Specificity for different color bodies can be assessed. And, finally, effectiveness can be approximately judged.

Anion Resins. Anion resins produced great variations in results. All free residual chlorine was gone before the batch tests were begun, but nevertheless there often appeared to be an antagonistic reaction as the color in chlorine, hypo, and chlorine dioxide wastes often increased. Color in caustic and ditch wastes always decreased, sometimes by more than 70 percent.

Amberlite IRA-68. This resin was moderately effective on chlorine dioxide and caustic wastes. It had little effect on hypo and none at all on chlorine waste. Considering that ditch waste was 15 percent caustic and 85 percent chlorine waste, the expected color removal was computed to be 36 percent. As the measured color reduction of ditch waste was 35 percent (from Table 12) it is evident that only the caustic fraction of the waste was being sorbed.

In spite of its failure to sorb chlorine waste and its mediocre performance on other wastes this resin rated testing in a column because it is one of the two resins needed for the Desal process.

Amberlite IRA-93. This is a hard, strong macroreticular resin noted for its resistance to fouling and to chemical attack so it is surprising to observe an immediate color increase of more than 100 percent when it was exposed to chlorine waste as shown in Figure 20. A curve like this would be expected of a resin from which some colored component was quickly leached. A synergistic effect occurred with ditch waste where the small amount of caustic mixed with a large amount of chlorine waste effectively muzzled the initial color jump, and 81 percent of the color was removed. This was a greater color reduction than was obtained with any other waste.

Amberlite IRA-93 merits considerable attention in column tests. It appears to be effective for color reduction and Sanks and Kaufman (1965, 1966) found it to be both readily regenerated and resistant to fouling.

Dowex 11. This resin, too, caused an immediate, drastic increase in the color of all except caustic and ditch wastes upon which it had little effect. The pH increased from 7.6 to 8.3 but this is entirely insufficient to account for such a gross increase of color. Strong base resins require an excess of caustic for regeneration and they tend to foul irreversibly, so it seems unlikely that any of the strong base resins are economical. A possible use for such resins might be the lowest horizon of a multilayered bed. Until such use is contemplated, there is little reason to test this resin in column operation.

Dowex WGR. This resin had almost no effect upon any but chlorine waste for which the color was increased more than 100 percent. Most of the color reduction in chlorine dioxide occurred after three hours, so the kinetics are not attractive. As a color sorbent, this resin can be dismissed.

Duolite A-6. This resin gave the best overall performance of any. Color removals were at least 50 percent for all except hypo waste. The color in ditch waste was reduced 84 percent whereas the color reduction in chlorine and caustic waste (the two main ingredients of ditch waste) were reduced 60 and 77 percent respectively. Hence, mixing the wastes was clearly beneficial.

Duolite A-7. In general Duolite A-7 was inferior to Duolite A-6, but the A-7 was superior for treating hypo and caustic. As both Duolite A-6 and A-7 are similar in all but functional groups there is no reason to expect column tests to reverse the findings of the batch tests.

Duolite A-57. This resin had little effect on the wastes. It can be summarily dismissed.

Cation Resins. The cation resins in hydrogen form did not prove to be effective in sorbing color.

Dowex HCR-W. This resin is typical of the gel-type polystyrene-divinylbenzene resins so widely used for demineralization. It drastically increased the color of all wastes except caustic. There was no reason to test this resin in columns.

Duolite C-25D. This resin is like Dowex HCR-W except for its porous matrix. It requires less regenerant and rinse water than do gel-type resins. Some increase of color was found with chlorine waste. There was either a slight sorption of color from other wastes or no effect at all. Duolite C-25D appears to be superior for demineralization. But it is not an effective sorbent and column tests are not required for color sorbency.

Organic Sorbents. The synthetic organic sorbents exhibited various degrees of selectivity in sorbing color from wastes. None sorbed all wastes. All increased the color in one or more wastes, sometimes by significant amounts.

Amberlite XAD-2. This resin had but little effect on most wastes. After 2 hours the color in chlorine waste began to increase at an accelerating rate. There was no such effect in ditch waste. During the investigations of color sorbency, the extreme dependence upon low pH was unknown, and a decision was made to abandon further tests with Amberlite XAD-2. Later, a better resin, XAD-8, was developed, so there was no reason to reconsider the decision.

Duolite S-30. This resin sorbed 45 percent of the color from ditch waste during the 4-hour period, most of it within the first hour, so the kinetic characteristics are good. However the color of hypo increased about 100 percent, and the effects on other wastes were negligible. In neutral acid form, at least, the resin is not a particularly effective sorbent for these wastes. Further testing is not required.

Duolite ES-33. This resin resembles S-30 in performance but it was somewhat superior with every waste. It might prove to be a useful sorbent, but no further tests were made.

Duolite S-37. Of the several sorbent resins, this was the best except with chlorine waste. The removal of color from ditch waste reached 70 percent within an hour and 86 percent in four hours.

The matrix and functional groups of Duolite ES-33 and Duolite A-6 are similar and Duolite A-7 is similar to Duolite S-37. In free base form secondary amine functionality was better and in chloride form, a functional mixture of secondary and primary amines was better. More color was sorbed from ditch waste by S-37 than by any other resin or carbon.

Carbon. Carbon sorbed color more uniformly than did resins. Color never increased. The best results were obtained with chlorine, hypo, and chlorine dioxide wastes and the poorest results were experienced with caustic and ditch wastes. These results are opposite to those obtained with resins which suggests that resins and carbon would complement each other.

The carbon was pretreated by being shaken in distilled water (to reduce abrasion during the tests), washed, and drained. The weight of carbon (and resin) per flask was 5 grams on a saturated, drained basis. The moisture varied from 53 to 86 percent of the dry weight which corresponds to carbon dry weights of 3.3 to 2.7 grams. While this compares resins and carbon on the same basis, it is awkward for comparison on the basis of purchase price. Were the tests to be run again the carbon would be weighed dry and presoaked afterward.

Filtrasorb. This carbon, although very hard, abrades significantly during shaking, so it was necessary to filter the liquor to obtain a valid color reading. Sorbance of color increased with decreasing particle size. Nearly 100 percent of the color was sorbed from chlorine, hypo, and chlorine dioxide wastes. But it should be noted that none of these three raw wastes contained more than 150 CU.

Filtrasorb 300 seems to be the most popular size in industrial use. It combines good kinetic properties with ease of handling and resistance to abrasion. It contained 74 percent water when loaded so the dry weight was 2.9 grams. Had 2.1 grams more dry carbon been loaded, it would have further reduced the color of caustic from 44 percent to about 65 percent. (This figure is based on calculations using a Freundlich isotherm which fits sorbency over a four-hour time period quite well.) The 67 percent reduction of color in ditch waste would have been 80 percent on the same basis.

Filtrasorb 400 was the best of all carbons tested. Sorption of color from chlorine, hypo, and chlorine dioxide wastes was essentially 100 percent. As loaded, the moisture content was 77 percent so the dry weight was 2.8 grams. Had the dry weight been 5 grams the color reduction of 67 and 75 percent for caustic and ditch waste respectively would have been 87 and 94 percent respectively. As this was the best of the carbons, it was chosen as the basis for comparison with resins.

Nuchar. Nuchar carbons performed about the same as Filtrasorb carbons. Nuchar WVL was slightly superior to the others except for the sorption of color in ditch waste. Its overall performance was nearly equal to Filtrasorb 400.

Lime Precipitation

The purpose of lime precipitation experiments was to provide enough information to select an optimum lime dose for producing a good supernatant liquor. No attempt was made to optimize massive lime flocculation because this has been thoroughly studied by the National Council for Stream Improvement (1962). Several forms of lime were tried: lime slurry, 60 percent lime mud, and reburned lime. The liquors were limited to caustic waste, ditch waste, and artificial ditch waste.

Lime Slurry. Lime slurry obtained from the mud washer with a moisture content of 278 percent (dry basis) was only moderately effective in removing color from caustic waste. Reductions in color of 41 and 76 percent were obtained with 50 grams dry mud/liter and 100 grams dry mud/liter respectively. Because far better results were obtained with reburned lime, experiments with lime slurry were discontinued.

Lime Mud. Lime mud cake (or 60 percent lime mud) obtained from the microscreen following the mud washer was tested on caustic and ditch waste with indifferent results. At a dosage of 10 grams dry mud/liter only 14 percent of color was removed from ditch waste. With massive amounts of mud 97 percent of the color could be removed. Color in caustic waste was reduced 25 percent with 50 g dry mud/liter and 61 percent with 100 g dry mud/liter.

In previous investigations, Sanks (1969) found lime mud to be much more effective. This is not surprising because its chemical characteristics are likely to vary considerably. But variations, if large, preclude its use in a process unless: (1) it always occurs in excess, (2) its effect can be reliably monitored, and (3) its dosage can be controlled by an automatic, feed-forward mechanism.

Experiments at the Hoerner Waldorf plant in 1965 which showed a 1/4 inch cake of lime mud removed 90 percent of the color from ditch waste prompted a few exploratory experiments with a filter leaf using lime and lime mud. Usually cakes built up to 1/4 inch within 20 seconds but occasionally it required as much as 60 seconds. Cracking time was always less than 15 seconds. However, the National Council for Stream

Improvement (1962) stated the cake tends to crack on microscreen drums permitting color leakage and furthermore vacuum filtration is expensive compared to sedimentation. For these reasons the experiments with filtration were not pursued beyond an exploratory phase.

Lime. By a wide margin, reburned lime was the most effective coagulant for the removal of color. The experiments with lime, summarized in Tables 13 to 16, indicate color removals in excess of 95 percent are readily achieved with the massive lime precipitation method patented by Berger et al (1964). The plant can produce enough lime (290 tons CaO/day maximum) to dose the waste caustic extract (460 gpm) at 106,000 mg/l. The same quantity of lime would dose the entire waste stream of 3390 gpm at 14,200 mg/l. The quantity of CO_2 required for recarbonation was measured but the data are omitted because correlation between model (a one-liter cylinder) and prototype is too uncertain. Suffice it to say the Hoerner Waldorf plant produces so much stack gas (16 percent CO_2 and 84 percent air) the amount required to reduce the pH to 7.6 is but a fraction of production.

The following explanation clarifies some of the data given in the tables. The reburned lime contains some impurities, so only about 90 percent is CaO. Doses are given as CaO rather than as gross weight. The mud depth ratio is the depth of precipitate divided by total depth of mud and liquor after two hours of settling in a one-liter cylinder. The carbon dioxide gas was bubbled until the pH fell to 7.6 but due to problems of mixing in a one-liter cylinder, the final pH of the mixed liquor sometimes differed from pH 7.6 by as much as pH 0.2. The percent color removal was based on the color of the waste neutralized to pH 7.6. A pH of 7.6 corresponded closely to the average pH of the Clark Fork River. Also pH 7.6 was readily achieved but pH values much less than that required excessive time and volumes of gas.

TABLE 13

COLOR PRECIPITATION FROM CAUSTIC WASTE WITH LIME

Caustic		Reburned lime	
Original pH	11.42	CaO, %	90
Color at pH 7.6, CU	18,200		
TDS, mg/l	4,330		
Ca as $CaCO_3$, mg/l	54		
Hardness as $CaCO_3$, mg/l	150		

Jar No.	1	2	3	4	5
Lime dose, g/l CaO	0	25	50	100	200
pH	11.40	12.22	12.20	12.23	12.40
Sludge depth ratio	-	0.11	0.16	0.27	0.88
Gas to pH 11.5:					
Color, CU at pH 11.5	18,200	3,835	1,140	830	220
Appearance of supernatant	opaque	clear	turbid	turbid	clear
Alkalinity, mg/l as $CaCO_3$	1,396	3,050	3,786	5,424	6,751
Calcium, mg/l as $CaCO_3$	54	480	570	497	144
Hardness, mg/l as $CaCO_3$	150	1,254	1,536	1,244	430
Gas to pH 7.6:					
Appearance	opaque	clear	clear	clear	clear
Color, CU	17,920	1,950	545	460	155
Color removal, %	0	89	97	97	99
TDS, mg/l	4,308	4,364	5,008	7,740	9,212
Alkalinity, mg/l as $CaCO_3$	1,469	1,862	2,370	3,127	6,960
Calcium, mg/l as $CaCO_3$	67	14	6	7	200
Hardness, mg/l as $CaCO_3$	170	36	18	22	203

TABLE 14

COLOR PRECIPITATION FROM DITCH WASTE WITH LIME

Jar No.	1	2	3	4
Lime dose, g/l CaO	0	1	2.5	5
pH	8.1	11.8	12.1	12.3
Sludge depth ratio	-	0.06	0.06	0.07
Gas to pH 11.5:				
Color, CU at pH 11.5	4,420	380	300	275
Appearance of supernatant	opaque	slt tur[a]	slt tur	slt tur
Alkalinity, mg/l as $CaCO_3$	403	1,053	1,985	2,630
Calcium, mg/l as $CaCO_3$	301	881	1,816	2,440
Hardness, mg/l as $CaCO_3$	385	953	1,885	2,460
Gas to pH 7.6:				
Appearance	opaque	clear	clear	clear
Color, CU	4,420	300	140	125
Color removal, %	-	93	97	97
TDS, mg/l	1,904	1,544	1,524	1,608
Alkalinity, mg/l as $CaCO_3$	370	283	300	355
Calcium, mg/l as $CaCO_3$	329	182	183	198
Hardness, mg/l as $CaCO_3$	395	205	218	215

Ditch waste	
Original pH	8.1
Color at pH 7.6, CU	4,420
TDS, mg/l	4,452
Ca as $CaCO_3$, mg/l	301
Hardness as $CaCO_3$, mg/l	385

Reburned lime	
CaO, %	90

[a] Slightly turbid

TABLE 15

COLOR PRECIPITATION FROM ARTIFICIAL DITCH WASTE WITH LIME

Jar No.	1	2	3	4	5
Lime dose, g/l CaO	0	2.0	3.0	4.0	5.0
pH	5.05	12.15	12.70	12.25	12.34
Sludge depth ratio	-	0.05	0.05	0.04	0.05
Gas to pH 11.5:					
Color, CU at pH 11.5	1820[a]	450	365	320	260
Appearance of supernatant	clear	clear	clear	clear	clear
Alkalinity, mg/l as $CaCO_3$	14	1730	2125	2150	2745
Calcium, mg/l as $CaCO_3$	146	1828	2220	2278	2810
Hardness, mg/l as $CaCO_3$	190	1830	2260	2260	2810
Gas to pH 7.6:					
Appearance	clear	clear	clear	clear	clear
Color, CU	1820[a]	180	100	100	75
Color removal, %	0	90	95	95	96
TDS, mg/l	887	1352	1316	1336	1372
Alkalinity, mg/l as $CaCO_3$	14	235	230	318	262
Calcium, mg/l as $CaCO_3$	146	300	290	280	235
Hardness, mg/l as $CaCO_3$	190	384	360	382	338

	Caustic	Chlorine	Lime
Constituent, %	20	80	--
Lime, % CaO	--	--	90
Original pH	10.42	2.56	
Color at pH 7.6, CU	18,200	253	
TDS, mg/l	4,330	2	

[a] pH 5.05

TABLE 16

COLOR PRECIPITATION FROM CHLORINE, HYPO AND CHLORINE DIOXIDE WASTES WITH LIME

Waste	Chlorine		Hypo		Chlorine Dioxide	
Original pH	3.72		9.30		7.25	
color at pH 7.6, CU	520		180		380	
Lime dose, g/l CaO	2	5	2	5	2	5
Appearance at pH 7.6	cloudy	cloudy	clear	clear	clear	clear
Color after recarbonation to pH 7.6, CU	240	70	0	0	0	0
Color removed, %	74	85	100	100	100	100

Significantly, the optimum dose of lime to declorize caustic extract waste was less than the entire lime budget of the plant. About half of the lime budget, or 50,000 mg/l reduced the color 97 percent, produced little more than the minimum obtainable TDS (total dissolved solids), and gave a low mud depth ratio. As shown by Figure 26 doses less than 50,000 mg/l were much less effective. The sedimentation rate of the 50,000 mg/l dose was near optimum whereas high doses resulted in much slower sedimentation rates as shown in Figure 27. Furthermore, both hardness and calcium remaining in the supernatant liquor were at or near the theoretical minimum after recarbonation to pH 7.6 as shown by Figures 28 and 29. The calcium lost in the supernatant liquor at this dosage would amount to only about 0.1 ton as CaO per day in plant operation.

Ditch waste, which varied greatly but was essentially 15 percent caustic extract and 85 percent chlorine waste was of an entirely different character than either of its two main constituents. As shown by Table 14 and Figure 30, the amount of lime required to reduce color in 3390

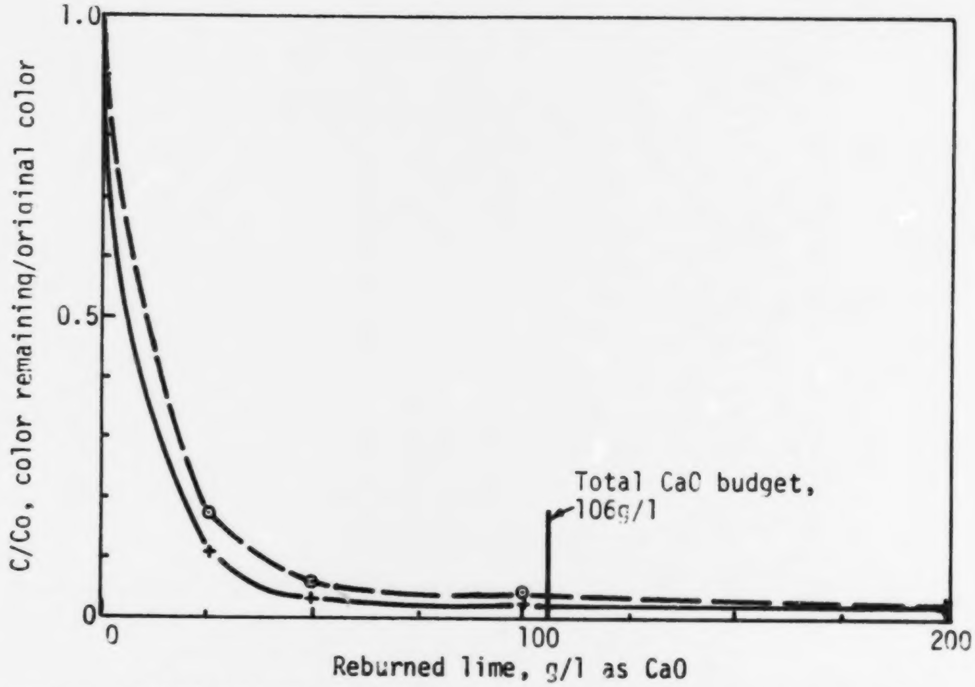

FIGURE 26. COLOR REMOVAL FROM CAUSTIC EXTRACT BY LIME PRECIPITATION

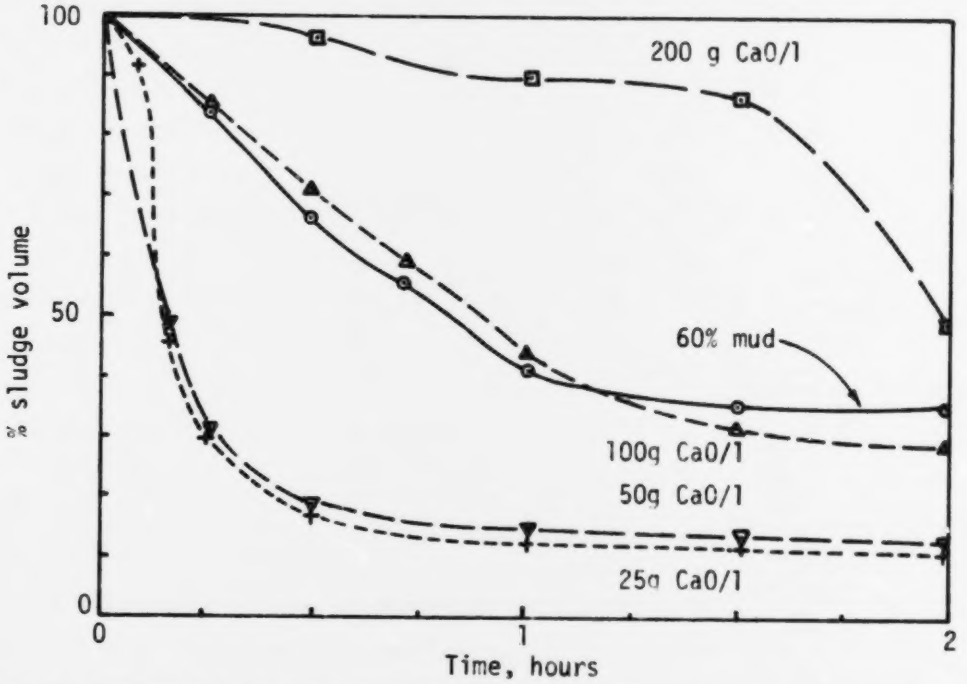

FIGURE 27. CAUSTIC EXTRACT SEDIMENTATION RATES IN LIME PRECIPITATION

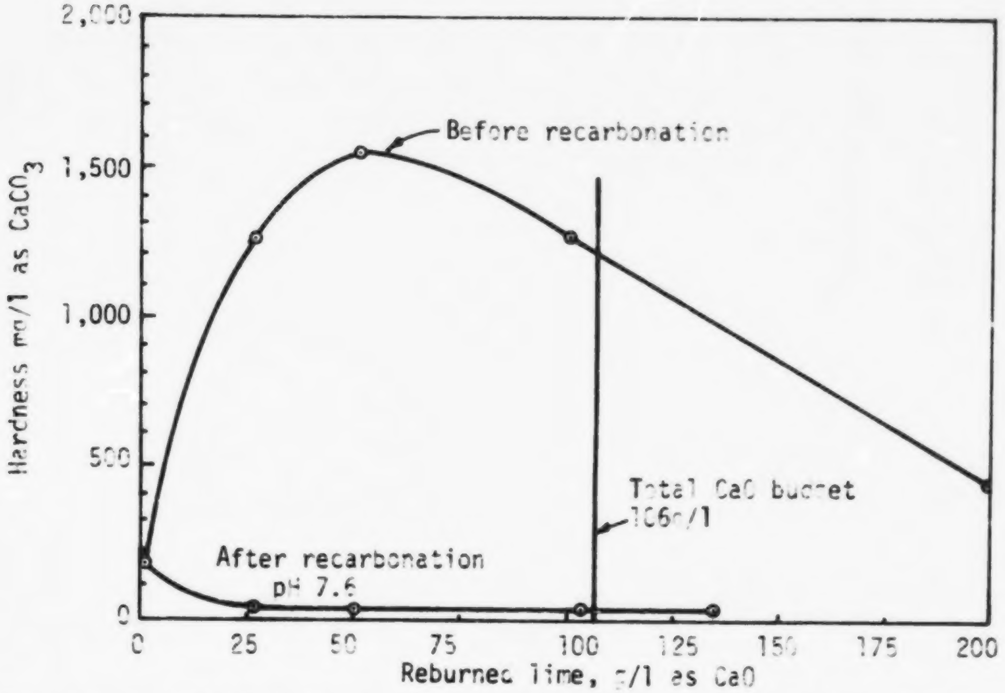

FIGURE 28. HARDNESS AFTER LIME PRECIPITATION OF CAUSTIC EXTRACT

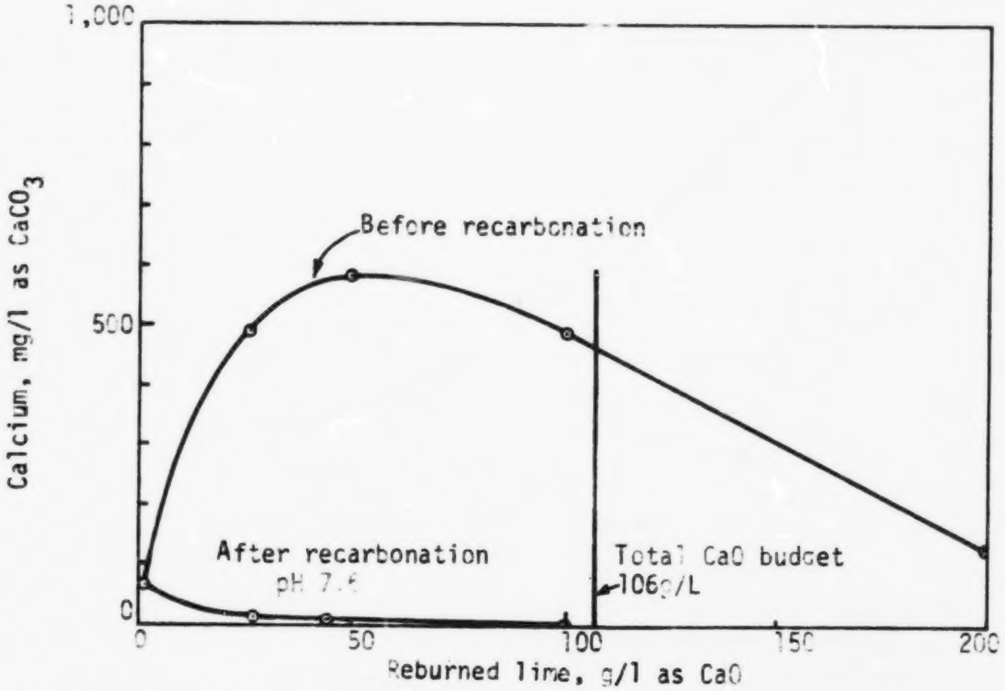

FIGURE 29. CALCIUM AFTER LIME PRECIPITATION OF CAUSTIC EXTRACT

gpm of ditch waste by 95 percent was less than required for 460 gpm of caustic extract. To reduce color by 95 percent in caustic extract required about 40 percent of the total lime budget of the plant. To reduce color by 95 percent in ditch waste requires about 1,200 mg/l or nearly 9 percent of the lime budget. Furthermore, the residual color in the treated ditch waste was less than 300 CU whereas if untreated chlorine waste were to be blended with precipitated caustic extract, the final color would be about 600 CU. Hence, it appears massive lime precipitation would be more effective if applied to ditch waste rather than to the caustic extract only.

In some plants, massive lime precipitation might interfere with recausticizing which could eliminate massive lime precipitation as a color control method. But it might not be difficult for such plants to carry a lime budget increase of about 10 percent for precipitation. The findings reported herein, if consistent, are significant.

Plots of sedimentation rates in Figure 31 show there is little choice between the various dosages. All precipitates settled well. After recarbonation to pH 7.6 the supernatant liquors for all doses were clear and the floc settled quickly.

The removal of hardness and especially of calcium after recarbonation, shown in Figures 32 and 33, was poor in this experiment. About 180 mg/l of calcium remained in the supernatant liquor after recarbonation. The process is the same as the well-known and commonly used excess lime softening process in which hardness can be commercially reduced to 80 mg/l as $CaCO_3$ at 20°C, and it should not be difficult to reduce the calcium content of the ditch waste to such a value. As the calcium content of the untreated ditch waste was about 300 mg/l, some lime could be recovered by this process.

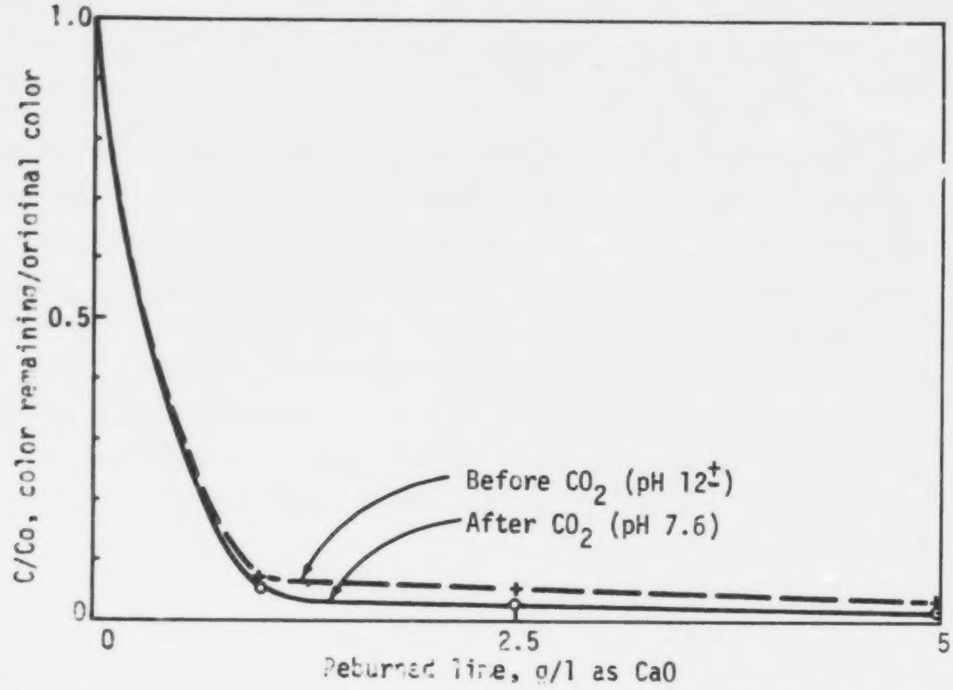

FIGURE 30. COLOR REMOVAL FROM DITCH WASTE BY LIME PRECIPITATION

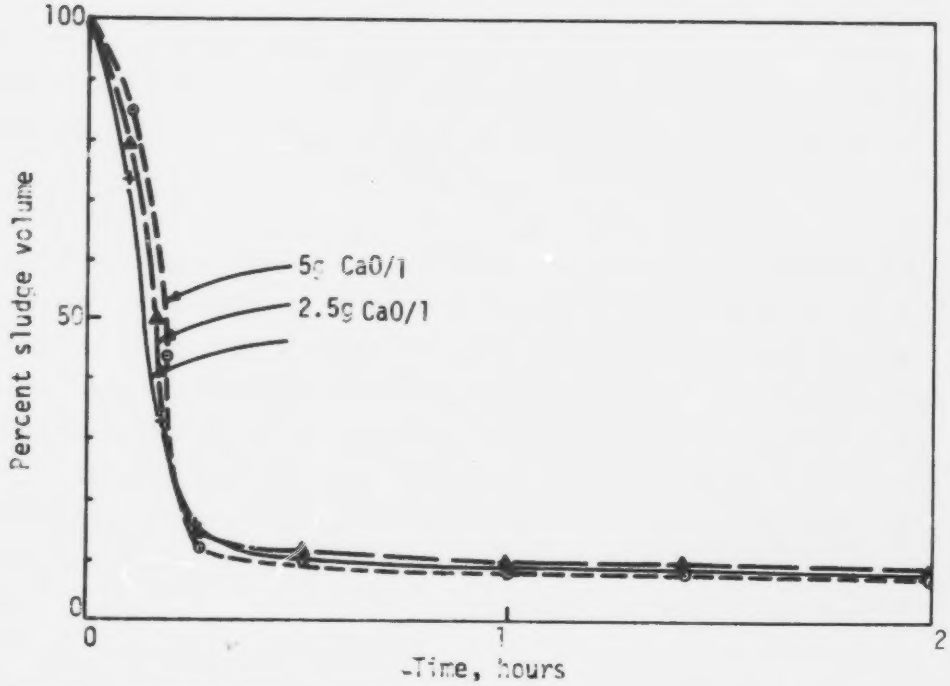

FIGURE 31. DITCH WASTE SEDIMENTATION RATES. LIME PRECIPITATION

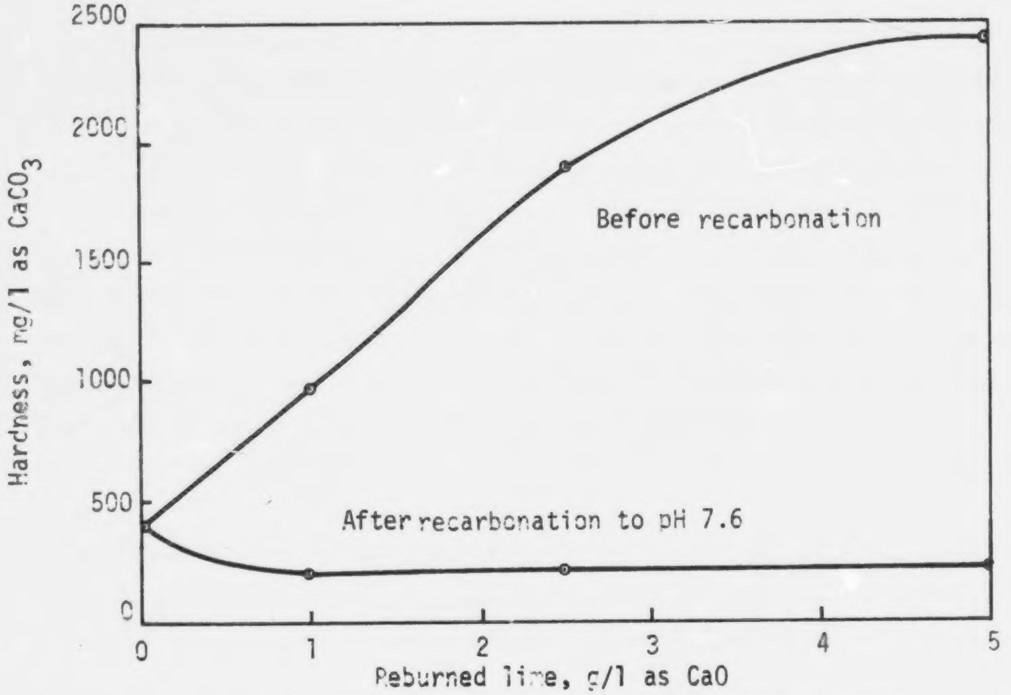

FIGURE 32. HARDNESS AFTER LIME PRECIPITATION OF DITCH WASTE

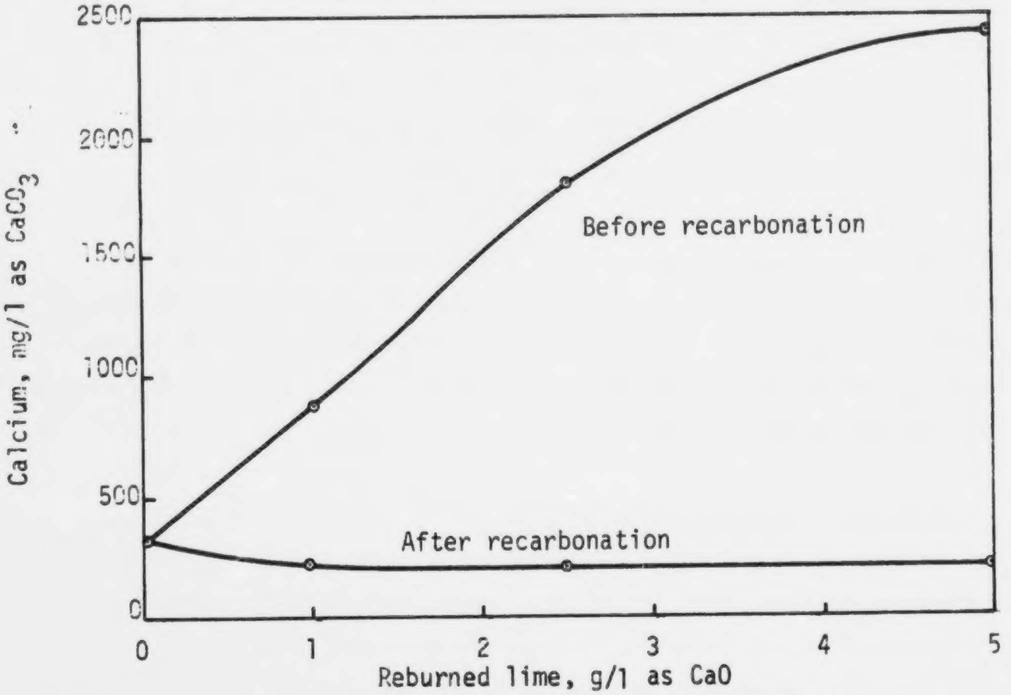

FIGURE 33. CALCIUM AFTER LIME PRECIPITATION OF DITCH WASTE.

Anomalies and variations experienced with ditch waste prompted making an artificial ditch waste. The first artificial ditch waste was made of 20 percent caustic extract and 80 percent chlorine waste to give a calculated color of 3,730 CU to approximate the real ditch waste. But the measured color, as shown in Table 15, was only 1820 CU. When the pH of both wastes was adjusted to 7.6 before mixing, the calculated and measured colors were the same. Apparently, the acid-base reaction of the raw wastes profoundly affected the color bodies. Later, artificial ditch wastes contained 15 percent caustic extract and 85 percent chlorine waste.

As Table 15 indicates, the dose of lime required to reduce the color by 90 percent was about 20 percent of the lime budget. Mixing the waste liquors before decoloring was advantageous.

As the liquor from the chlorine, hyopchlorite, and chlorine dioxide stages is returned to the process in counter-current flow, none of it except accidental spills or minor leaks goes to waste. Hence experiments with flocculation of these wastes were only exploratory. The procedure was the same employed in testing caustic and ditch wastes, and Table 15 summarizes the effects on color.

Small amounts of lime (2000 mg/l or less) removed 100 percent of the color of hypochlorite and chlorine dioxide liquors but 5000 mg lime/l resulted in only 85 percent reduction of color from chlorine waste. However, none of the raw wastes are highly colored, so a color reduction of 85 percent produces a nearly colorless product.

Color Sorbency After Lime Precipitation

The National Council for Stream Improvement (1967) stated carbon is uneconomical for the removal of concentrated color and its role is logically one of polishing effluents after most of the color is removed by massive lime precipitation. Certainly, very large amounts of carbon are required to decolor raw ditch wastes. Obviously, decolorization by chemically regenerated sorbents is only feasible if little or no product water is required for regeneration and rinsing. The efficiency of carbon and resins for polishing the effluent from the precipitation process is explored in this section.

Waste. Tests of lime-precipitated waste were confined to caustic extract because it is the most troublesome fraction. It contains the most color and even after lime precipitation, it was still more highly colored than the other raw wastes except ditch wastes.

Lime precipitation of caustic extract was repeated several times. Inevitably, there were slight variations in the percentage of color removed, and hence there were variations in the initial color of the various batches of waste.

Resin. Typical time-sorbency curves are shown in Figure 34. Table 17 shows the color and total organic carbon remaining after four hours of sorption.

Lime precipitation clearly has benefits that reach beyond gross color removal. The performance of resins in removing color from raw caustic waste is poor as can be seen in Figures 7, 9, 11, 19, 20, and 21. But the percentage removal of color from lime-precipitated caustic waste is fair to excellent. For example, Dowex 11 at a dose of 5 g/100 ml removed only 17 percent of color from untreated caustic. But even a dose of 1 g/100 ml removed 100 percent of the color from lime-precipitated caustic.

Table 17 shows the best performance was obtained with Dowex 11 followed in order of merit by Amberlite IRA-93, Duolite A-57, Amberlite IRA-68, and Duolite A-6. The performance of Duolite S-37 was only fair with

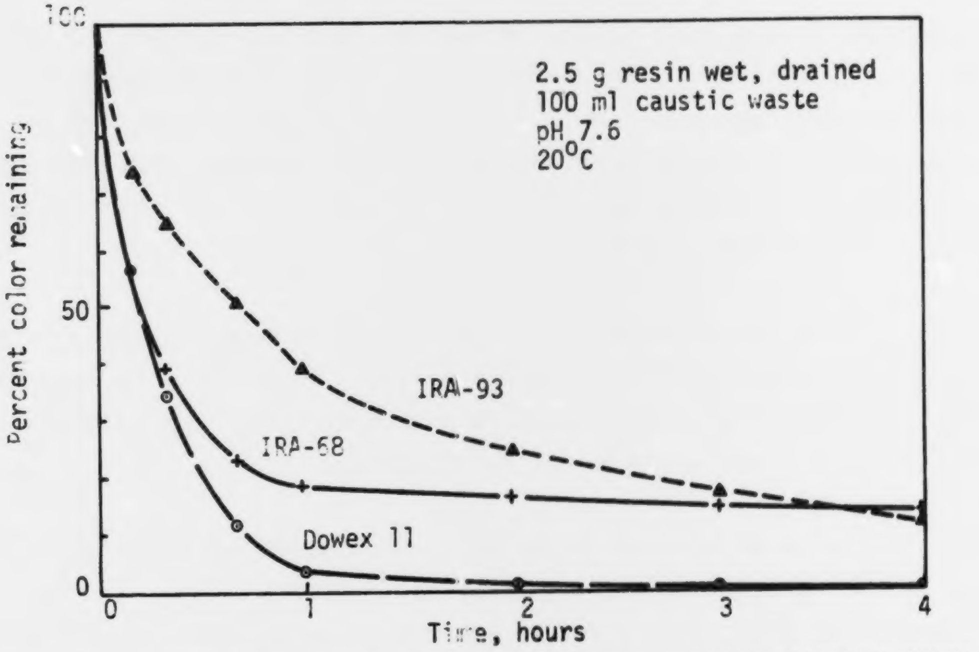

FIGURE 34. COLOR SORPTION OF LIME-PRECIPITATED CAUSTIC WASTE BY RESIN

TABLE 17

RESIN SORPTION OF CAUSTIC COLOR AFTER LIME PRECIPITATION

		Color after precipitation:		450 CU	
Untreated color:	18,200 CU	Color removal by precip:		97.5%	
Lime dose:	35g CaO/1	TOC after precipitation:		725 mg/1	
		After 4 hrs. sorption			
				Removals, %	
Sorbent	Dose g/1	Color, CU	TOC, mg/1	Color	TOC
Amberlite IRA-68	1	60	600	87	17
	2.5	55	600	88	17
	5	50	575	89	21
Amberlite IRA-93	1	80	565	82	22
	2.5	50	575	89	21
	5	0	575	100	21
Duolite A-6	1	80	600	82	17
	2.5	50	600	89	17
	5	70	575	85	21

(Table 17 continued)

Duolite S-30	1	395	525	12	28
	2.5	350	500	22	31
	5	290	500	36	31

		Color after precipitation:	360 CU
Untreated color:	18,200 CU	Color removal by precip:	99%
Lime dose:	50g CaO/1	TOC after precipitation:	725 mg/1

Amberlite XAD-2	1	305	640	15	12
	2.5	270	600	25	17
	5	240	600	33	17
Dowex 11	1	0	600	100	17
	2.5	0	540	100	26
	5	0	480	100	34
Dowex WGR	1	270	620	25	15
	2.5	270	640	25	12
	5	270	630	25	13
Duolite A-7	1	305	680	15	6
	2.5	445	600	-24	17
	5	700	580	-95	20
Duolite A-57	1	40	625	89	14
	2.5	35	625	90	14
	5	40	500	89	31
Duolite ES-33	1	250	600	31	17
	2.5	250	620	31	15
	5	285	600	21	17
Duolite S-37	1	150	625	58	14
	2.5	90	575	75	21
	5	90	600	75	17

85 percent of the color removed. Other resins such as Duolite ES-33, Dowex WGR, Amberlite XAD-2, and Duolite S-30 removed only 30 percent or less of the color, and Duolite A-7 increased the color somewhat.

Except for Amberlite IRA-93, the resins appeared to sorb color rapidly. Hence little color was sorbed after one hour of contact. A high rate of sorption is beneficial in column operation as it permits frequent regeneration which in turn tends to prevent blinding.

Removals of total organic carbon were low. Furthermore, there seems to be little correlation between color removal and TOC removal. Duolite S-30 removed little color but on the other hand, it performed better than other resins on TOC removal. The amount of TOC was not large and it is possible that some solvents or other organic material from the resin were dissolving in the liquor.

Table 17 shows occasional anomalies. Such anomolies can result from an error of only 1 percent on the transmittance scale of the spectrophotometer and such errors are occasionally to be expected. Anomalies in the values of TOC also occur and are not surprising considering the accuracy of the TOC analyzer in use at that time.

Carbon. Lime precipitation also benefited sorption of color by carbon and the carbons were very effective. Their rate of sorption was somewhat less than the rate of resins, but sorption was usually more complete as shown in Figure 35 and Table 18.

There was little difference between Nuchar and Filtrasorb. After four hours of sorption the color removal was independent of particle size. The removal of TOC was better and more consistent than removal by resins, but again there does not appear to be a direct relation between color and organic carbon.

GEL CHROMATOGRAPHY

Principle

Gel chromatography is a method for separating compounds of different molecular weights. The gel is a very porous material with holes of varying sizes. When mixtures of different compounds are eluted through the gel column, molecules larger than any of the holes will be found only in the surrounding liquid, whereas smaller molecules will exist

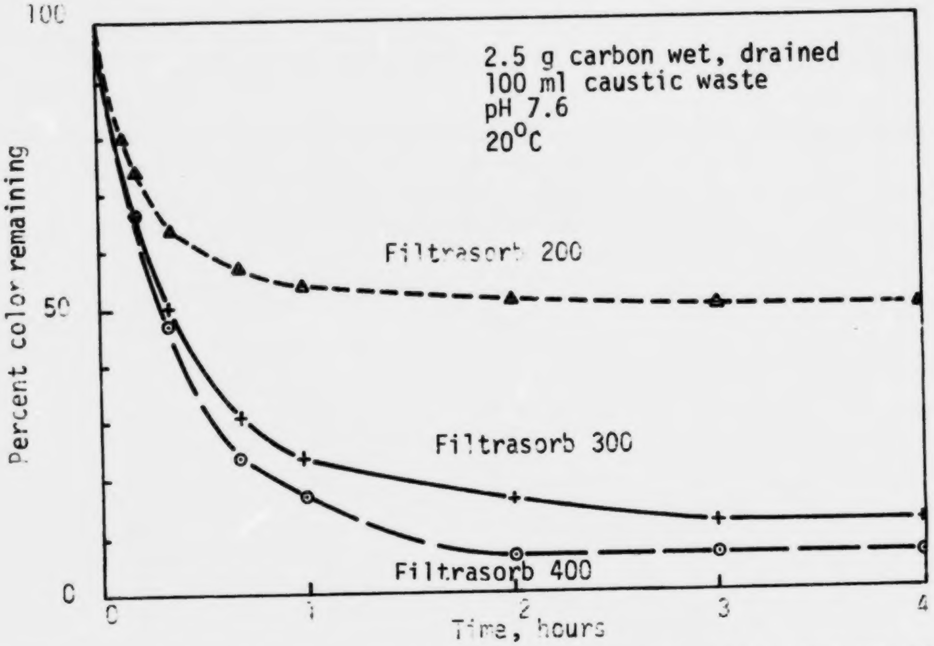

FIGURE 35. COLOR SORPTION OF LIME-PRECIPITATED CAUSTIC WASTE BY CARBON

not only in the surrounding liquid but also in pores larger than the size of the molecules. Hence, smaller molecules are dissolved in a larger volume of liquid and will be eluted later than larger molecules. All molecules will be eluted within the volume of the surrounding liquid and the pores because no ion exchange occurs. This volume is less than the total volume of the column by the true volume of solid material. Since molecular size generally increases with molecular weight, the method can be utilized to give a qualitative description of the distribution of molecular weights in a mixture.

TABLE 18

CARBON SORPTION OF CAUSTIC COLOR AFTER LIME PRECIPITATION

		Color after precipitation:	450 CU
Untreated color:	18,200 CU	Color removed by precip:	97.5%
Lime dose:	35g CaO/l	TOC after precipitation:	725 mg/l

			After 4 hrs. sorption			
		Dose			Removals %	
Sorbent		g/l	Color, CU	TOC, mg/l	Color	TOC
Filtrasorb	100	1	250	530	44	27
		2.5	70	500	85	31
		5	0	510	100	30
	200	1	240	570	47	21
		2.5	230	540	49	26
		5	0	500	100	31
	300	1	90	540	80	26
		2.5	55	500	88	31
		5	0	500	100	31
	400	1	25	540	95	26
		2.5	25	520	95	28
		5	0	500	100	31
Nuchar	WVG	1	50	580	89	20
		2.5	0	500	100	31
		5	0	470	100	35
	WVL	1	80	450	82	38
		2.5	0	450	100	38
		5	0	440	100	39
	WVW	1	200	470	56	35
		2.5	60	460	87	37
		5	0	460	100	37

Artificial Ditch Waste

The artificial ditch waste apparently consists of many different organic compounds because there were no real peaks except for very small molecules. These results were found also by Luner, Dence, Bennett, and Kung (1970). Loras (1965) found spent liquor from the chlorination of spruce sulfite pulp to have two principle fractions with weight-average molecular weights greater and smaller than 5000. By use of Sephadex G-50 and LH-20, Collins, Webb, Didwania, and Lueck (1969) were able further to fractionate molecular weights of less than 5000 in spent chlorination liquors from sulfite and kraft pulps.

The data of our studies show Duolite A-6 appears to remove some of the compounds of every weight but preferentially those just under a molecular weight of 1800.

Demineralization through Duolite C-25D and A-6 appears to remove more of the larger molecules than were removed by A-6 alone.

Filtrasorb 400 carbon columns appear to remove smaller molecules preferentially. Hence, it would appear advantageous to manufacture a resin which would remove all molecules with equal efficiency or else to combine resins (or resins and carbon) of complementary characteristics.

The results of gel chromatography, limited though they were, explains the failure of a sorbent to effect substantially greater reduction in color after the first pass through the resin.

COLOR SORBENCY IN COLUMNS

Column Size

An internal diameter of one inch is ordinarily considered to be minimum in ion exchange columns because of excessive wall effects for lesser diameters. But even one-inch columns require large amounts of feed. Were they reliable, half-inch columns would conserve liquor, so several runs were made to compare half-inch columns with one-inch columns. The resin beds in each were 24" deep and the flow rate in BV/hr were the same for both.

The feed for the columns was caustic bleach waste precipitated with approximately 35 grams of lime as CaO/1 and recarbonated to a pH of 7.6 with a concentration of about 300 CU. The flow rate was 20 BV/hr. Typical results, shown in Figures 36 and 37, indicate only a fair comparison between the half-inch and one-inch columns.

Several runs with Amberlite IRA-93 and Duolite A-6 are compared in Figures 38 and 39. The figures themselves and a regression analysis in which the coefficient of correlation is 0.97 with 13 degrees freedom in Figure 5, indicates the comparison to be rather poor. However, several different batches of wastes were used, so the comparison includes not only the size effect, but also the effect of variation in feed. Variations in feed greatly affect column performance and leads to a scattering of test results that are as important as the difference between half-inch and one-inch columns. Hence, it was concluded half-inch column tests are adequate but only for screening runs.

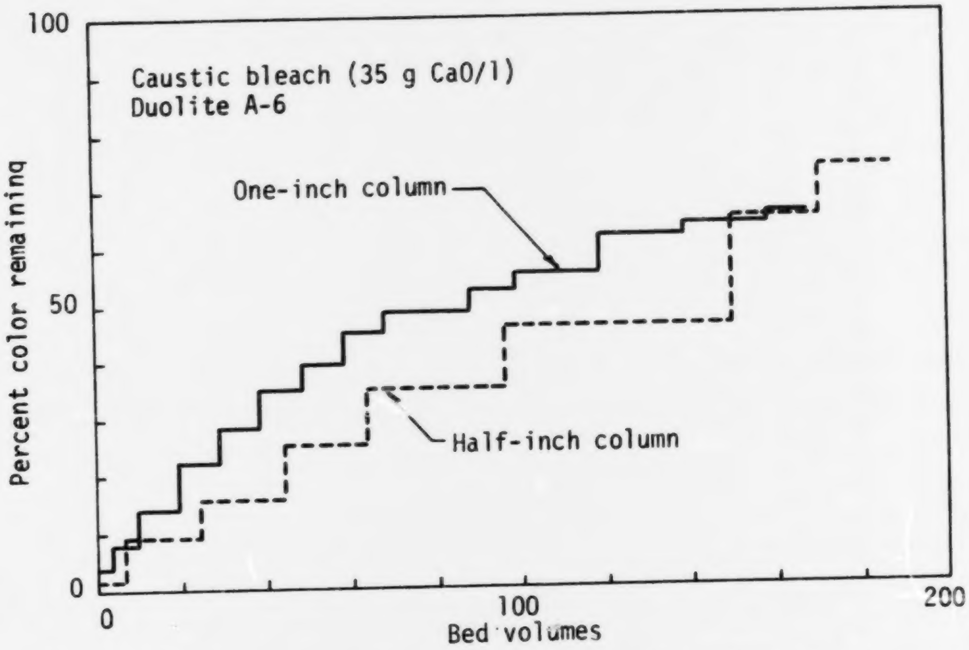

FIGURE 36. COLOR BREAKTHROUGH FOR HALF-INCH AND ONE-INCH COLUMNS

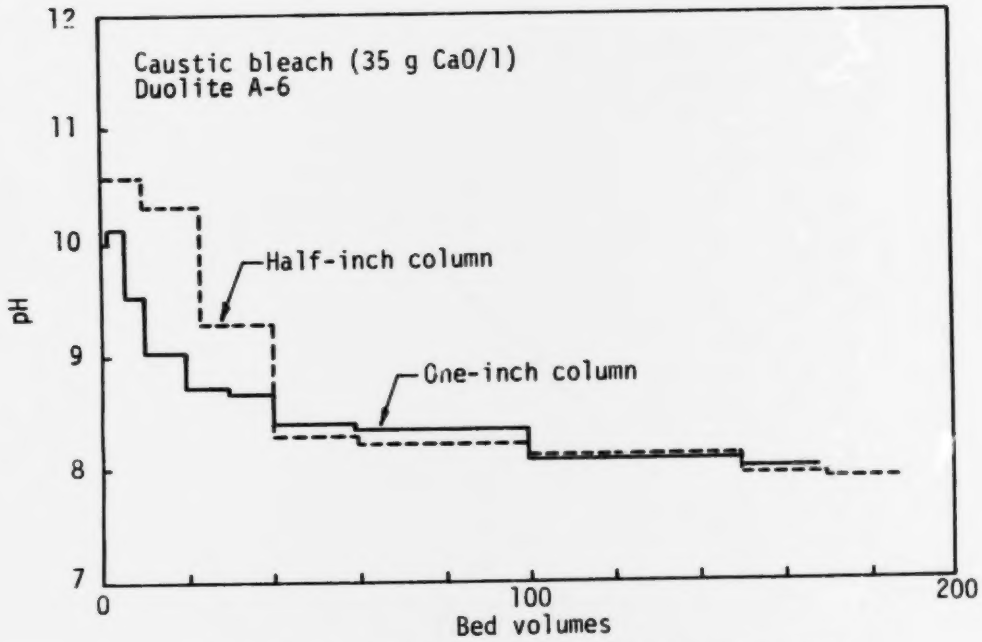

FIGURE 37. CHANGE OF pH FOR HALF-INCH AND ONE-INCH COLUMNS

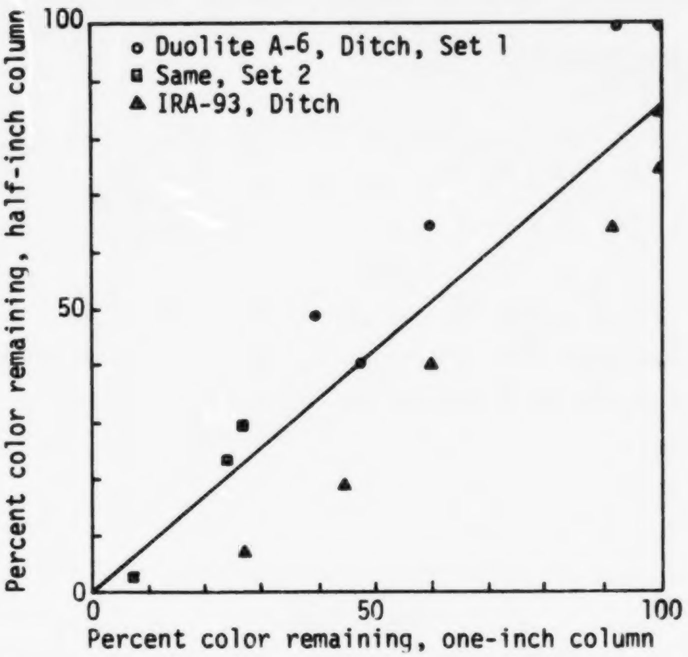

FIGURE 38. COMPARISON OF COLOR REMOVAL IN HALF-INCH AND ONE-INCH COLUMNS

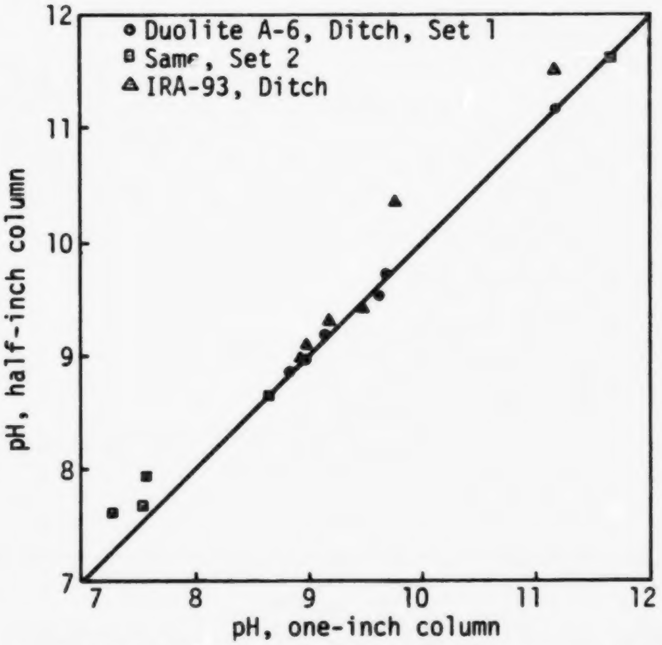

FIGURE 39. COMPARISON OF pH IN HALF-INCH AND ONE-INCH COLUMNS

Half-Inch Column Screening Runs

The screening runs comprised several series of fixed-bed ion exchange operations to compare the resins selected in batch studies for further study and to compare operating parameters and different wastes.

Flow rate for exhaustion. The effect of flow rate on color breakthrough is shown in Figures 40 and 41 for Duolite A-6 resin fed with ditch waste in which color was reduced to 275 CU by lime precipitation. There is no readily apparent optimum rate of flow. Sorption decreased more or less steadily with an increasing flow rate. The desirability of low flow rates is certainly evident from the standpoint of effectiveness of the resin, but on the other hand low flow rates result in large reactors and a large capital expenditure. As there is no evident optimum flow rate, 20 BV/hr (2.5 gpm/cu ft) was selected with consideration for operational efficiency and speed in performing laboratory runs.

Wastes. The countercurrent operation in the Hoerner Waldorf Mill discharges wastes only from the chlorine and the caustic extract stages. Approximately 15 percent of the waste is caustic extract and 85 percent is chlorine waste. As shown in Figure 5 the wastes from the other stages are recycled to the preceeding stage. Nevertheless, to obtain a better idea concerning the refractory character of other wastes, each waste was tested with each of the sorbents selected in batch tests for further study. These results are shown in Figures 42 to 46 and in Table 19.

In general, the waste most easily decolored was ditch waste followed by caustic extract. Hypochlorite, and particularly chlorine and chlorine dioxide liquors tended to be refractory. However, the juxtaposition of the different wastes were different with the various resins, which supports the supposition that resinous sorbents can be selected or even tailored to accomplish different jobs at different mills.

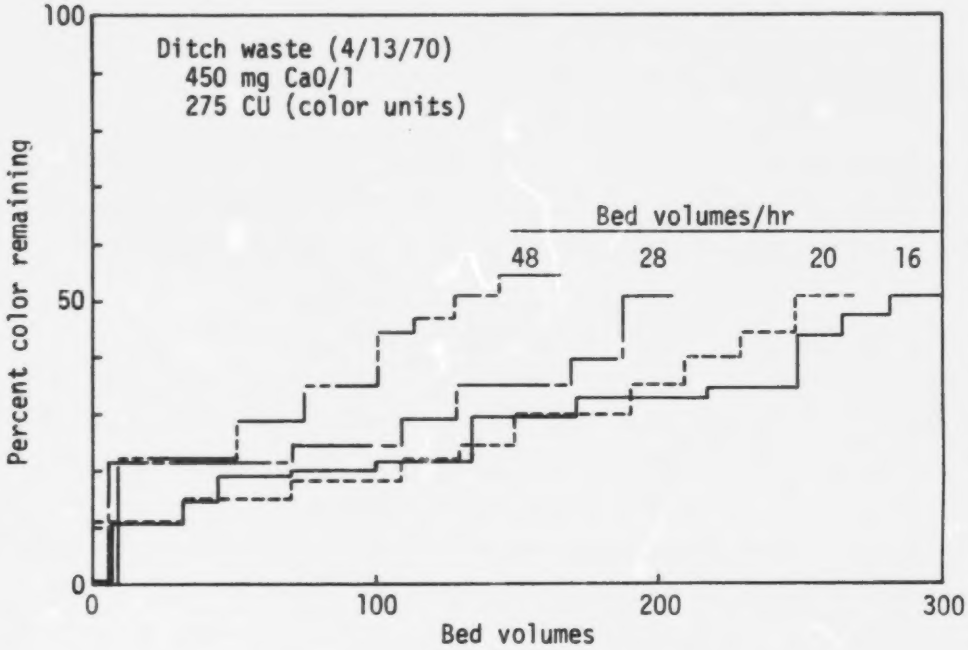

FIGURE 40. SORPTION OF COLOR AT VARIOUS FLOW RATES IN DUOLITE A-6 RESIN. HALF-INCH COLUMN

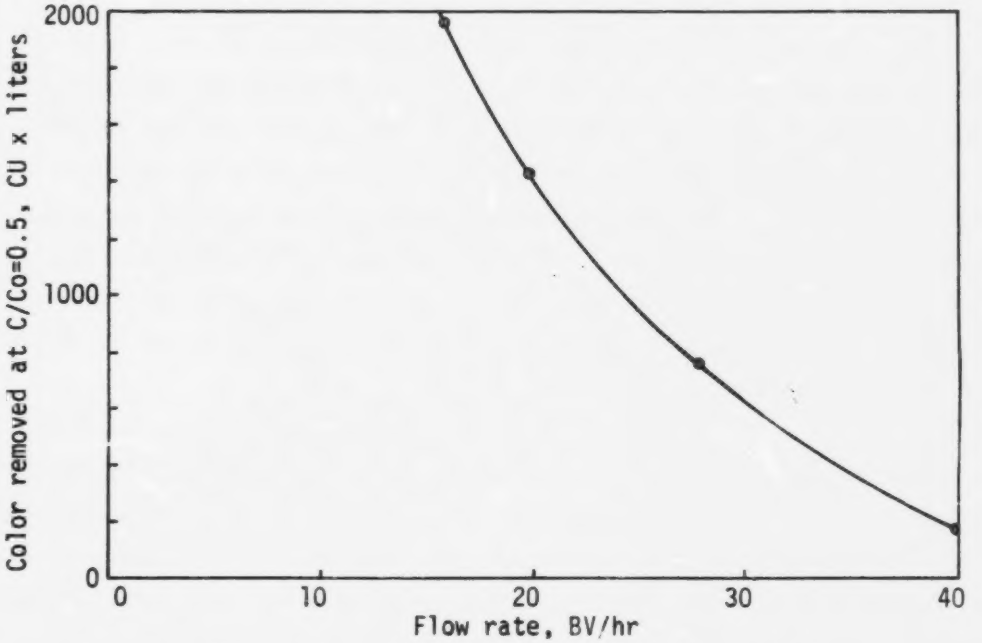

FIGURE 41. EFFECT OF FLOW RATE ON SORPTION. HALF-INCH COLUMN

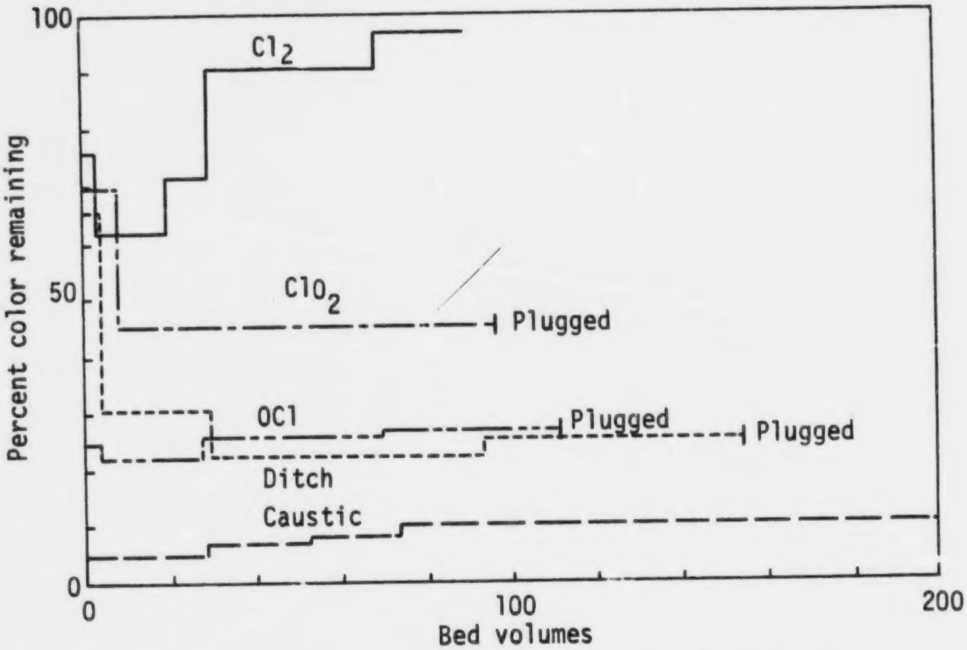

FIGURE 42. IRA-68 COLOR SORPTION. HALF-INCH COLUMN

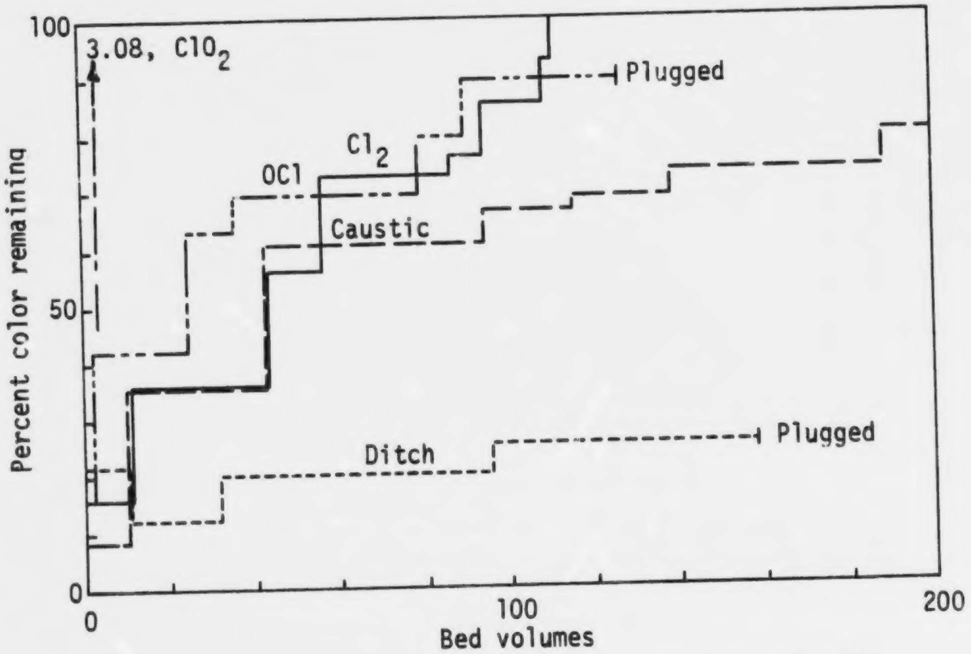

FIGURE 43. IRA-93 COLOR SORPTION. HALF-INCH COLUMN

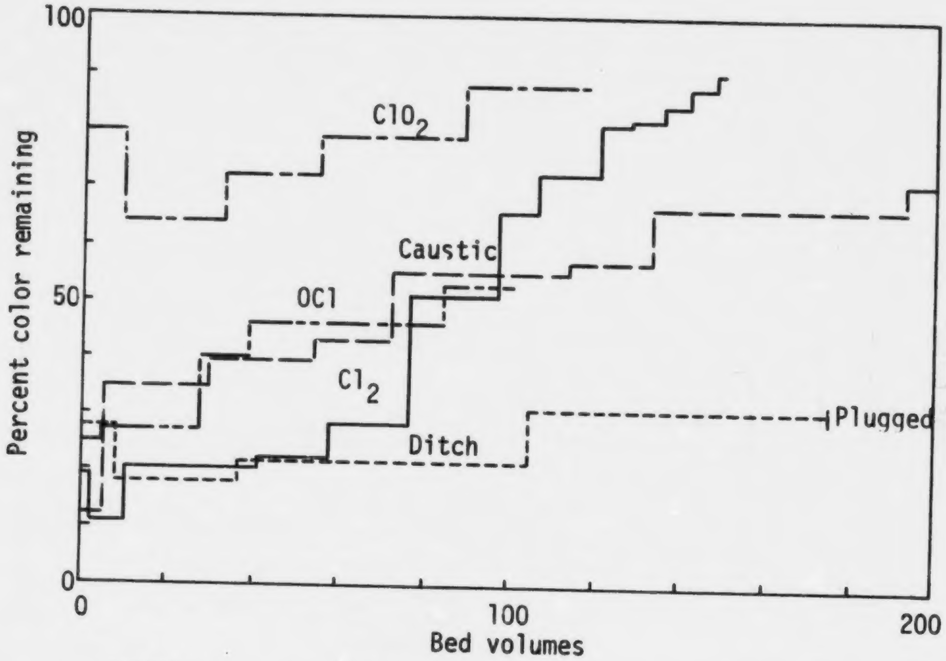

FIGURE 44. S-37 COLOR SORPTION. HALF-INCH COLUMN

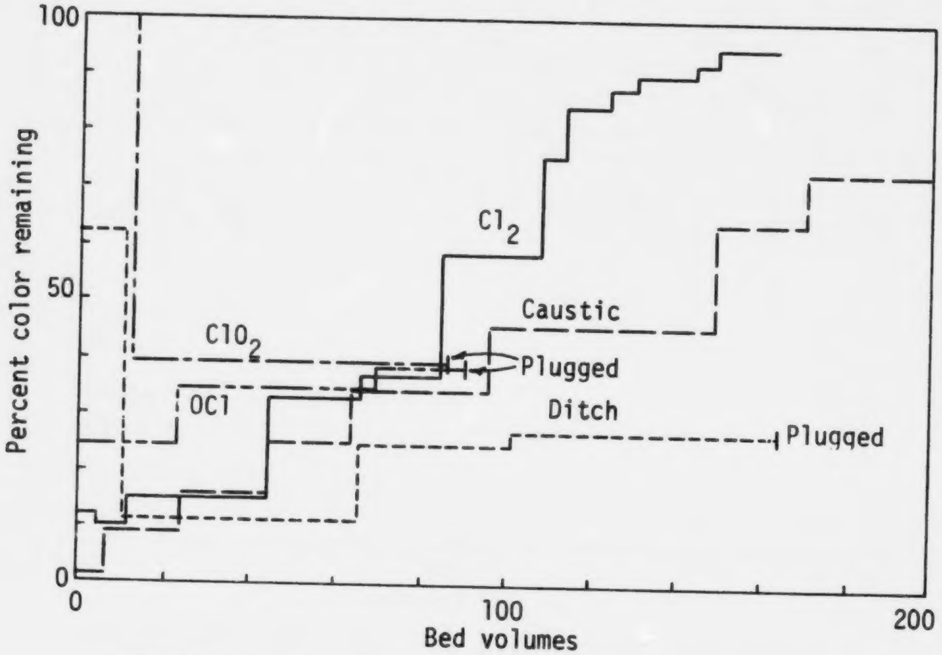

FIGURE 45. A-6 COLOR SORPTION. HALF-INCH COLUMN

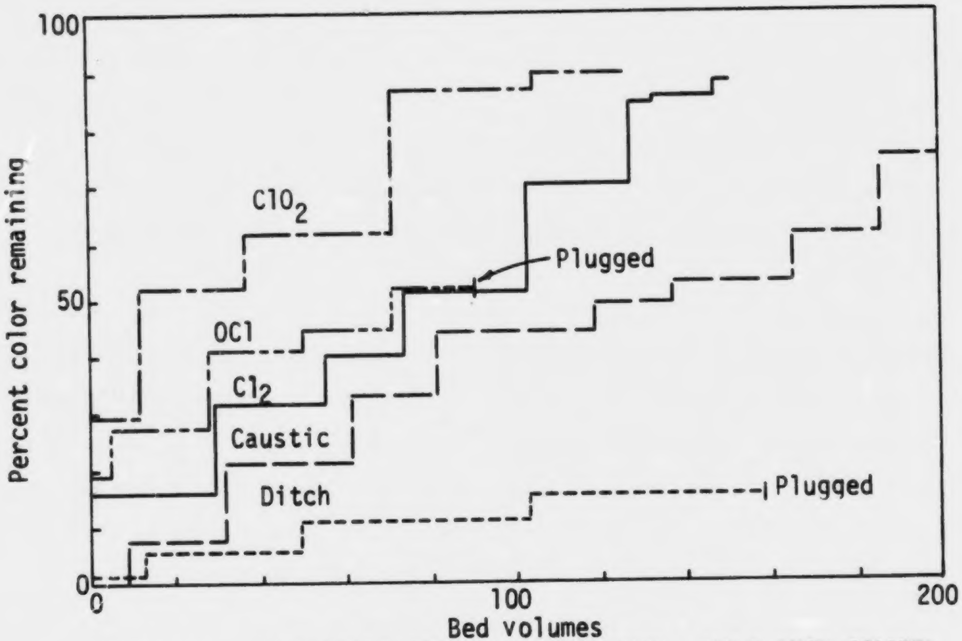

FIGURE 46. FILTRASORB 400 COLOR SORPTION. HALF-INCH COLUMN

TABLE 19

BED VOLUMES OF WASTE REQUIRED TO REACH COLOR BREAKTHROUGH OF 50%
(Half-Inch Column)

	Waste				
Sorbent	Cl_2	Caustic	ClO_2	OCl	Ditch
IRA-93	44	80	1	22	160
IRA-68	1	200	100	110	150
S-37	84	95	1	88	180
A-6	80	145	90	95	165
Filtrasorb 400	82	138	25	70	160

Sorbents in virgin state. In half-inch column runs, carbon performed better than did resin sorbents on ditch waste. But IRA-68, IRA-93, S-37, and A-6 resins also performed well. IRA-68 resin was by far the most effective sorbent for removing color from caustic waste followed by A-6 resin and carbon. The other sorbents were less effective.

A-6 and IRA-68 resins were superior for chlorine dioxide waste whereas the other sorbents were relatively ineffective. Amberlite IRA-68 also appeared to be the best resin for sorbing color from hypochlorite. However A-6, S-37 and carbon appeared to be almost as effective as IRA-68. The best sorbents for removing color from chlorine waste were S-37, A-6, and carbon. The other sorbents were poor.

Because of the time required to make the column runs and because the liquors needed for the runs were augmented by newly flocculated and recarbonated batches from time to time, the comparison of sorbents is not completely definitive. Furthermore, as explained above, the half-inch columns tend to give rather wide variations in results. Nevertheless the screening runs show ditch waste is more readily decolored than are other wastes and all of the sorbents are reasonably competitive for ditch waste. Evidently color in other wastes is preferentially sorbed in different order by the different resins. Resins are also competitive, in general, with carbon for color sorption from liquors other than ditch waste.

One-Inch Colunn Runs

Virgin resins. All five sorbents (IRA-68, IRA-93, S-37, A-6, and Filtrasorb 400 carbon) were tested in this series. The only feed used was ditch waste in which approximately 90 percent of the color was removed through massive lime precipitation followed by recarbonation to pH 7.6. In the first two sets of experiments, the remaining color, 280 CU versus 450 CU, varied by 50 percent. (Afterward it was possible to obtain a residual color of exactly 300 CU.) But the first two batches of wastes produced anomalies which could not be accounted for by the difference in residual color. Each of the two batches were used for one-inch column runs and the first batch gave good correlation with the previous half-inch column runs as shown by a comparison of Figures 47 and 48 with Figures 42 and 43. The second batch with the higher residual color gave abnormally short column runs as shown by Figures 49 to 51.

Because of the evident difference between the two feeds used in this phase of the investigation it is dangerous to compare all sorbents on the same basis. Nevertheless it is possible to conclude that the performance of IRA-68 is nearly identical with that of IRA-93. S-37 was somewhat more effective than A-6 and both were superior to Filtrasorb 400 carbon.

Regeneration With White Liquor

The general purpose of this phase of the work was to establish the feasibility of using white liquor to regenerate resin columns in single runs. The white liquor was used as received from the Hoerner Waldorf Mill or diluted to less than its natural concentration of 3 normal as required. The resins, partly exhausted with lime-flocculated ditch waste, were divided into packets of 28 ml to make resin beds one inch in diameter and one inch deep.

The regeneration of each of three resins, Duolite A-6, Duolite S-37, and Amberlite IRA-68, was optimized in single runs with respect to three variables: concentration of regeneration, flow rate, and amount. To save time and liquor, regeneration experiments were carried out in columns one inch in diameter and one inch deep. For evaluating relative performance, such a column size is entirely adequate.

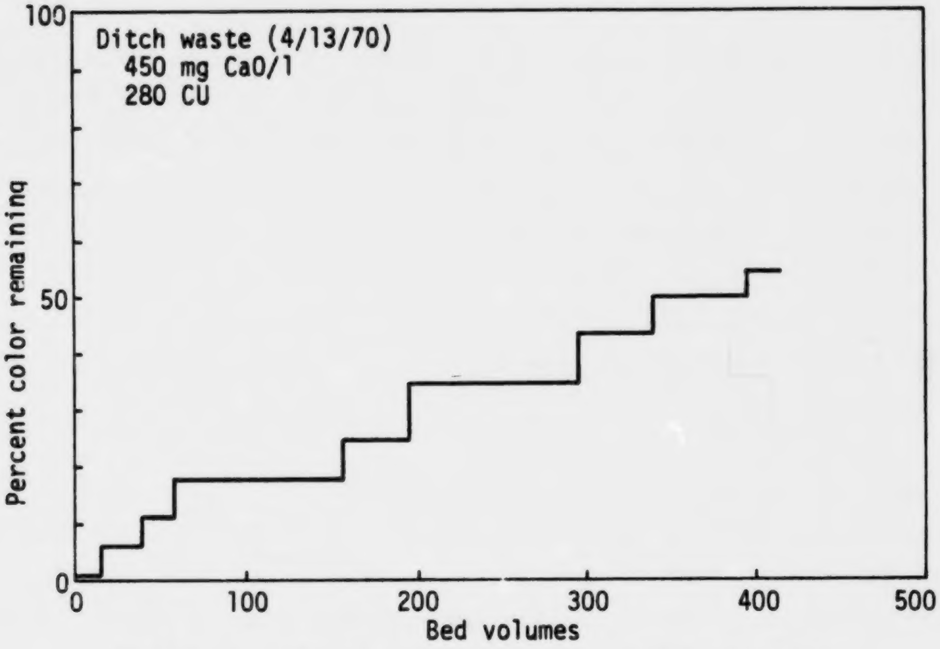

FIGURE 47. IRA-68 COLOR SORPTION. ONE-INCH COLUMN

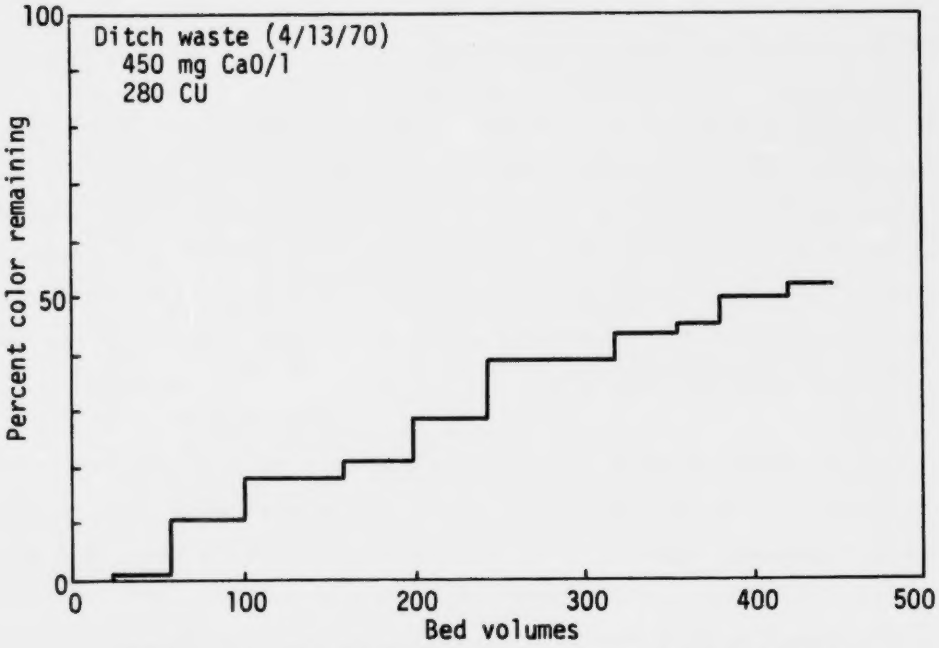

FIGURE 48. IRA-93 COLOR SORPTION. ONE-INCH COLUMN

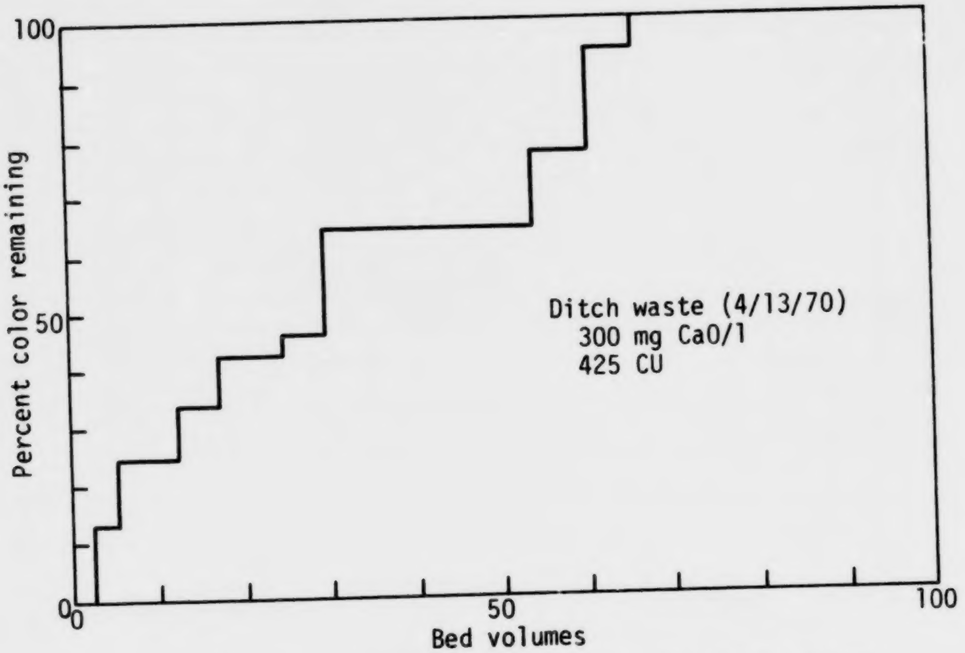

FIGURE 49. S-30 COLOR SORPTION. ONE-INCH COLUMN

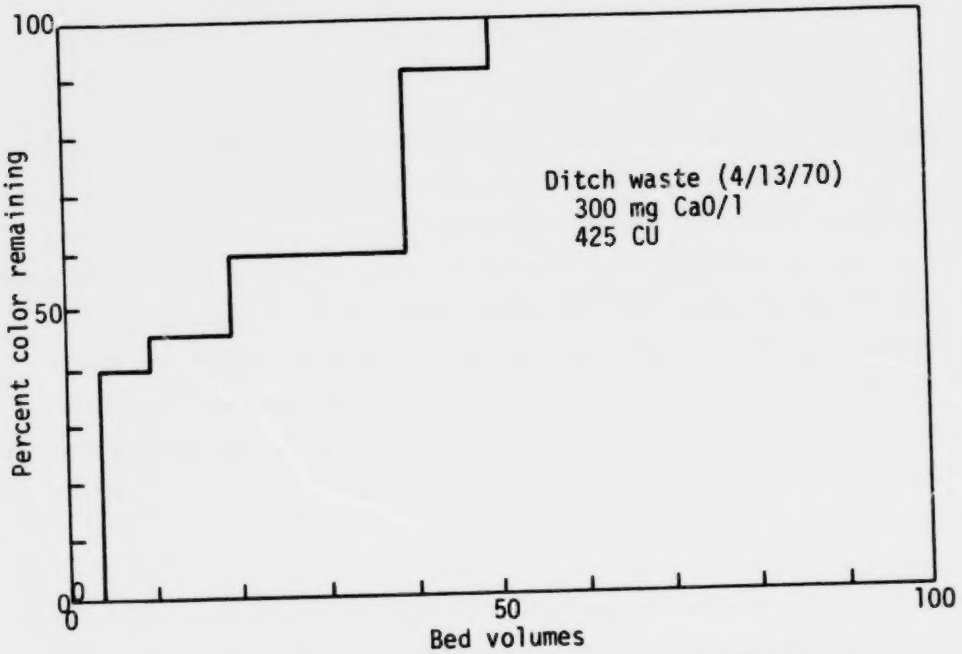

FIGURE 50. A-6 COLOR SORPTION. ONE-INCH COLUMN

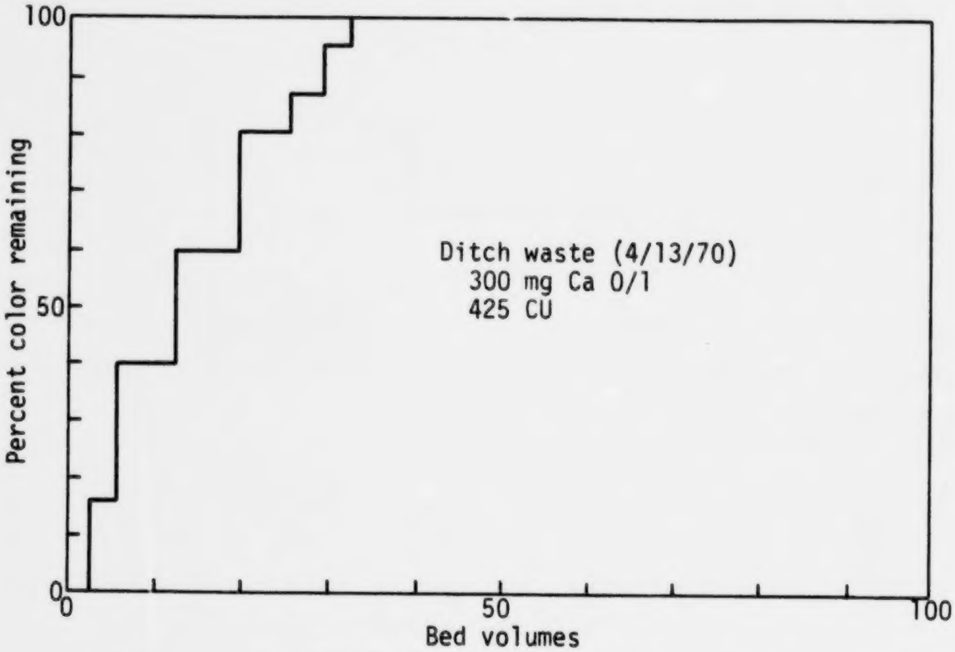

FIGURE 51. FILTRASORB 400 COLOR SORPTION. ONE-INCH COLUMN

Concentration. It is desirable to regenerate the resins with undiluted white liquor because the spent regenerant can then be transferred to the digesters with the rest of the white liquor. Such an operation would not interfere with mill operations and therefore the resins could be regenerated cheaply. On the other hand, if it is necessary to dilute the regenerant, some interference with mill operations would occur. Dilution of the process chemicals is, in general, critical. Although the effects of dilution of white liquor on the mill operations have not been investigated it seems nevertheless desirable to avoid any dilution.

In exploring the effect of the concentration of regenerant upon the efficiency of regeneration, all flow rates were 20 BV/hr. Therefore as the concentration was reduced the rate of application in me of NaOH per hour decreased.

As shown in Figures 52 and 53, undiluted white liquor at 3.0 normal was the best regenerant for Duolite A-6 resin. After regeneration with nearly 400 me the resin appeared to be like new. No signs of damage (such as physical disintegration) were detectable in these single runs.

As shown in Figures 54 and 55 Duolite S-37 appeared to be insensitive to concentrations between 1 and 3 normal. Concentrations less than 1 normal were less efficient. After regeneration the resin appeared to be like new with no visible damage.

Figures 56 and 57 show Amberlite IRA-68 is very sensitive to the concentration of the white liquor. The best concentration was 0.25 normal. The inefficiency of regeneration at higher concentrations can probably be explained on the basis of the high shrinkage observed at these concentrations which showed the resin matrix closed around the sorbed color bodies thereby decreasing the solid diffusivity. Inspection of the resin beads showed not all color was eluted from the resin at any of the concentrations or volumes of throughput investigated. The resin remained very dark.

The maximum amount of color eluted in these tests was 5,200 CU-liters with nearly 400 me of 3 normal caustic in Duolite A-6 resin. The most color removed from Duolite S-37 was 900 CU-liters with nearly 300 me of 1 normal caustic, and no more color could be eluted even with 700 me of 3 normal caustic. Although superficially Duolite A-6 appears to be superior to Duolite S-37, it may not be so because the A-6 was more completely exhausted than the S-37.

The maximum amount of color removed from Amberlite IRA-68 was about 330 CU-liters at a regeneration level of about 100 me of 0.25 normal white liquor. In single runs, at least, the regeneration of Duolite S-37 and A-6 was superior to Amberlite IRA-68.

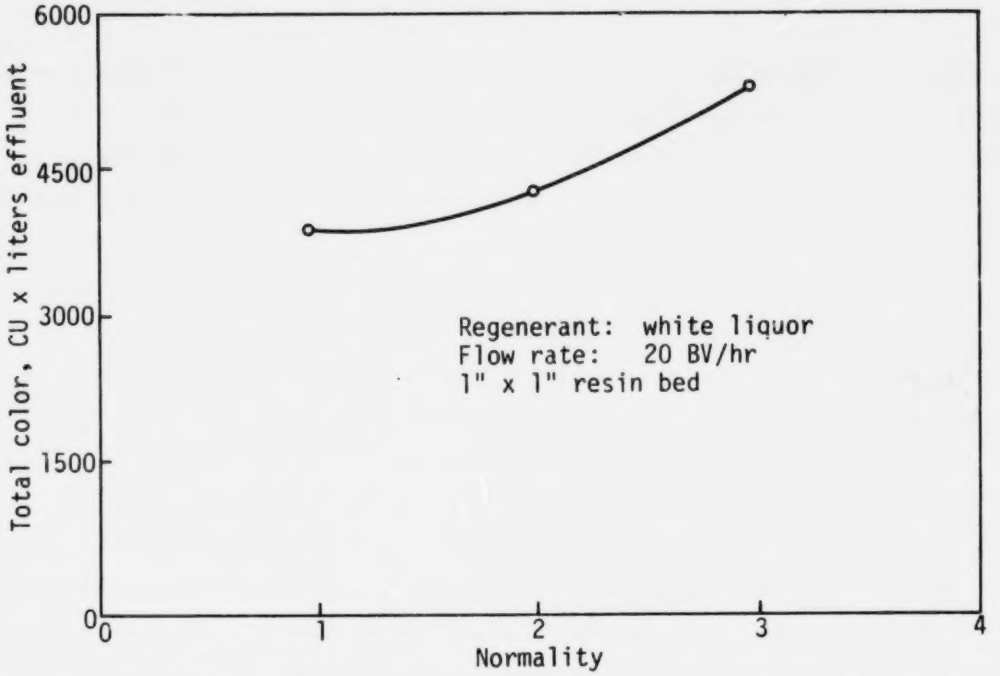

FIGURE 52. EFFECT OF CONCENTRATION ON REGENERATION OF A-6 RESIN

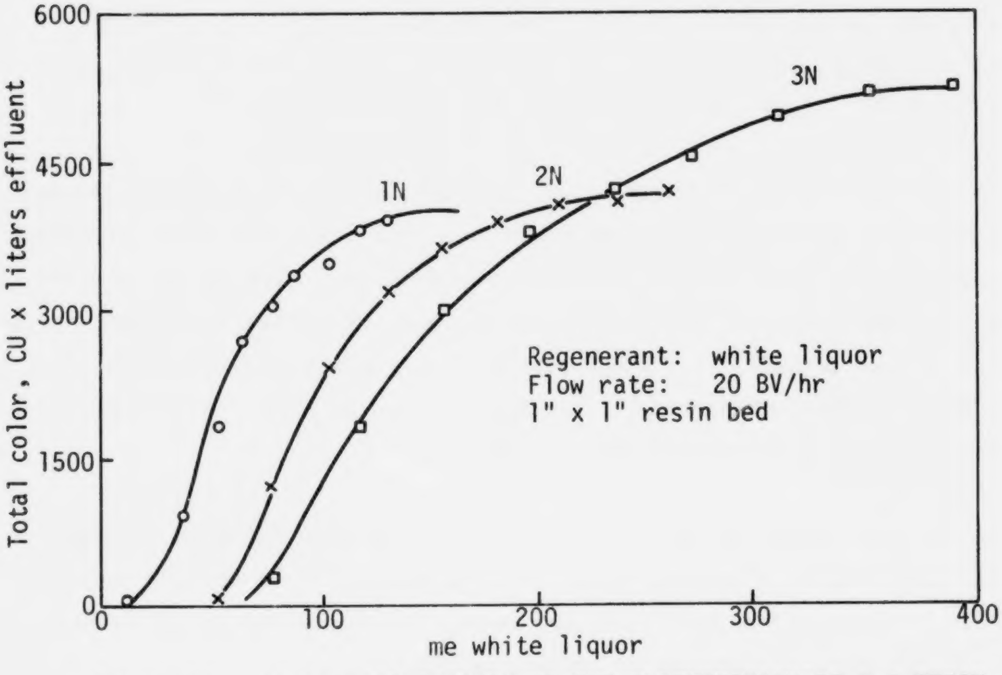

FIGURE 53. COLOR BREAKTHROUGH IN THE REGENERATION OF A-6 RESIN

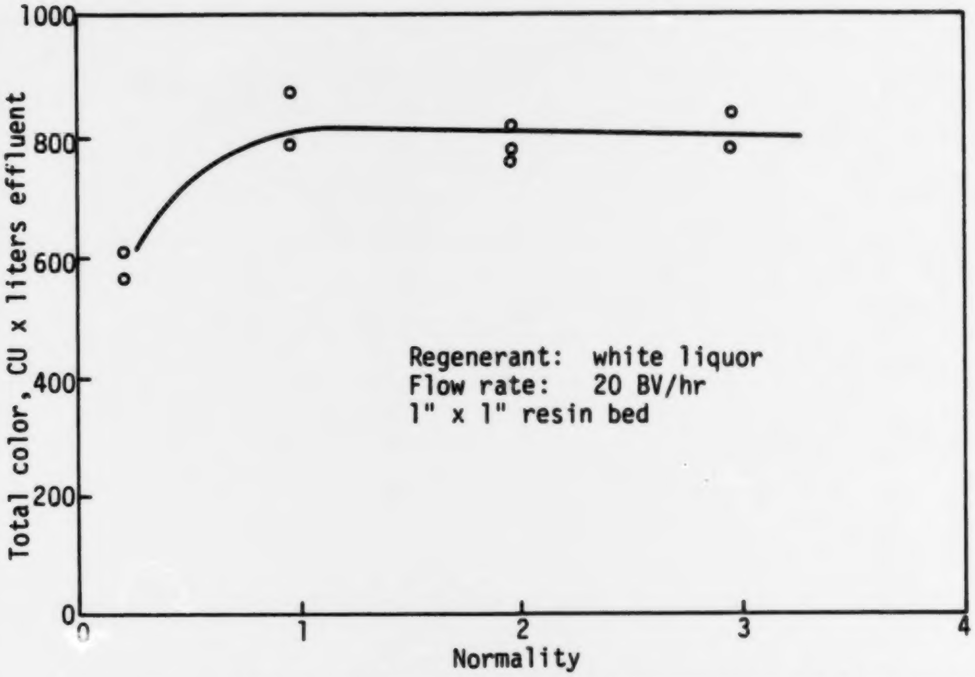

FIGURE 54. EFFECT OF CONCENTRATION ON REGENERATION OF S-37 RESIN

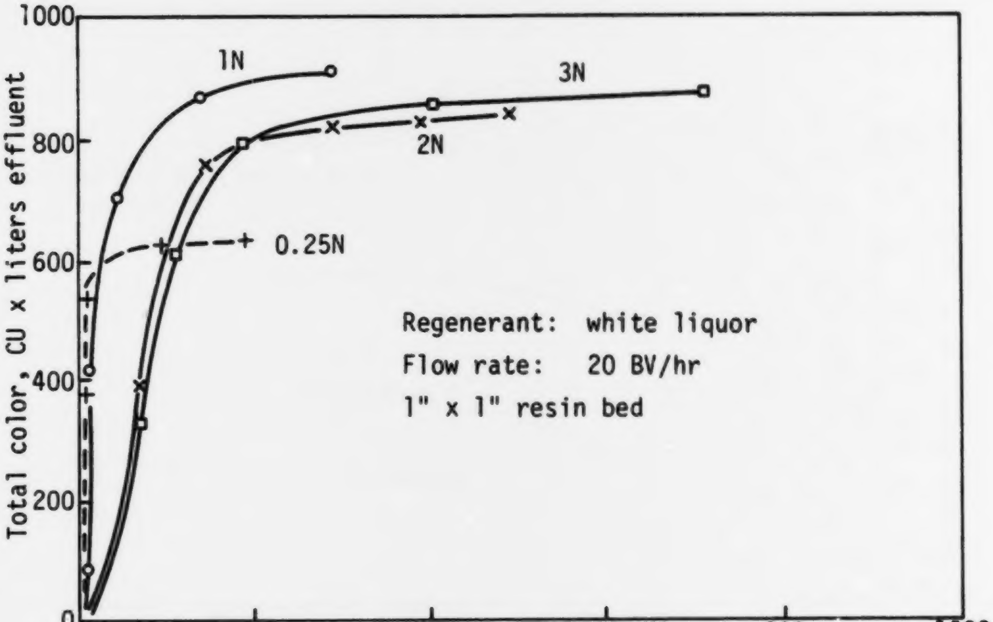

FIGURE 55. COLOR BREAKTHROUGH IN THE REGENERATION OF S-37 RESIN

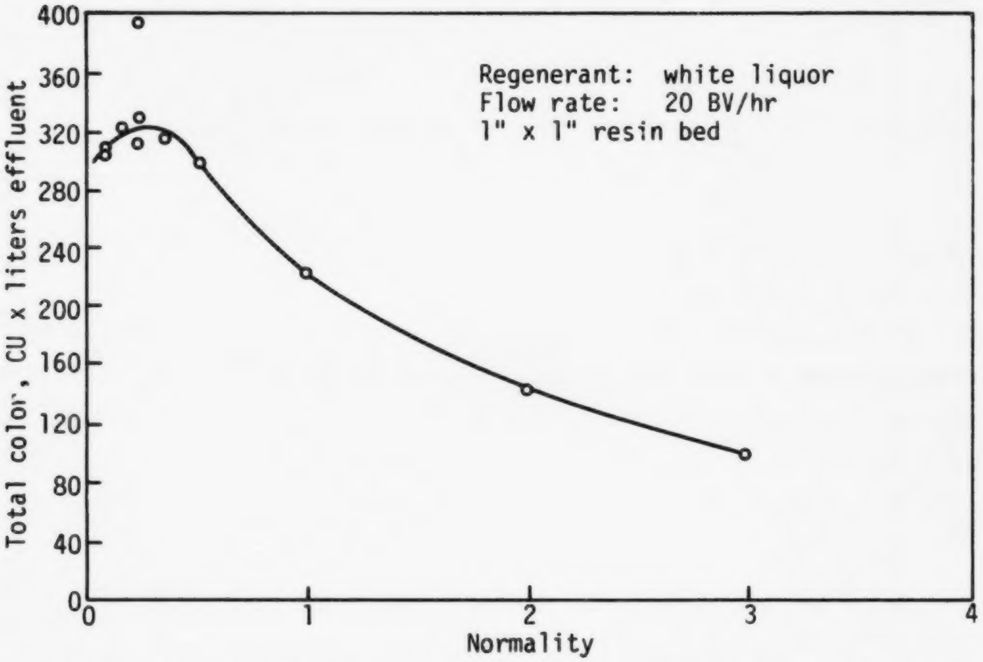

FIGURE 56. EFFECT OF CONCENTRATION ON REGENERATION OF IRA-68 RESIN

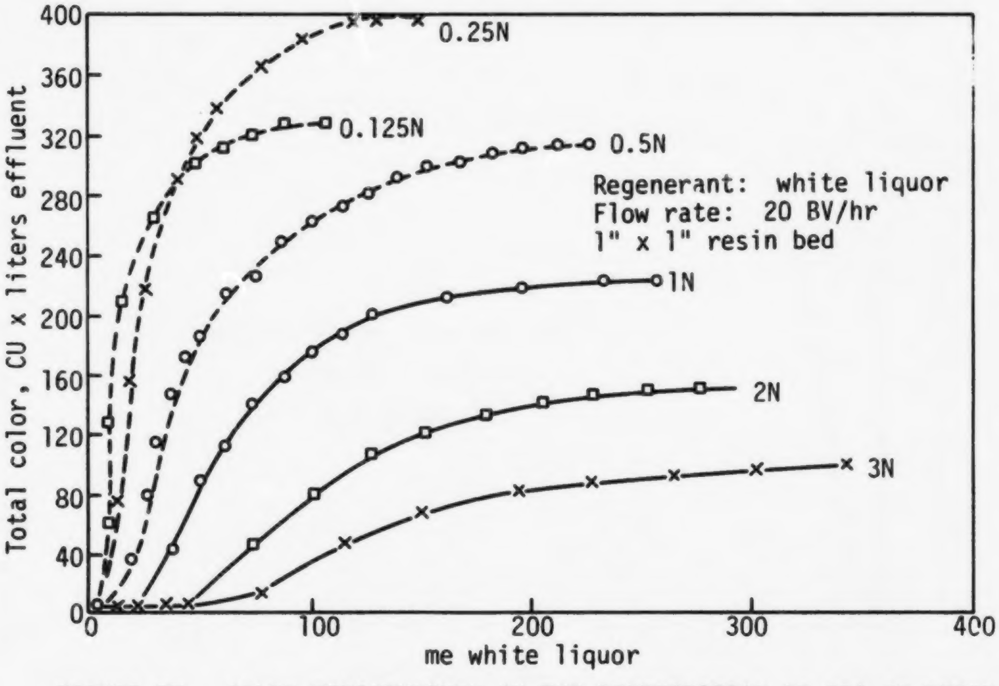

FIGURE 57. COLOR BREAKTHROUGH IN THE REGENERATION OF IRA-68 RESIN

Flow rate. The effect of flow rate upon regeneration efficiency was determined using the optimum concentration of regenerant for each resin, namely: 3.00 normal white liquor for Duolite A-6 and Duolite S-37 and 0.25 normal for Amberlite IRA-68 resin.

As shown in Figure 58 the optimum flow rate for Duolite A-6 was 5 BV/hr. However at flow rates of 7 to 25 BV/hr, the efficiency was nearly as great. Beyond a flow rate of 25 BV/hr and below 5 BV/hr the efficiency decreased. These results appeared to be somewhat anomalous, but corroborating runs were made with confirming results. Glueckauf (1955) has shown theoretical considerations can lead to peculiarities with respect to flow rates in resin columns. Because a flow rate of 5 BV/hr (which produced the highest efficiency) results in excessively long regeneration times, 25 BV/hr was considered optimum.

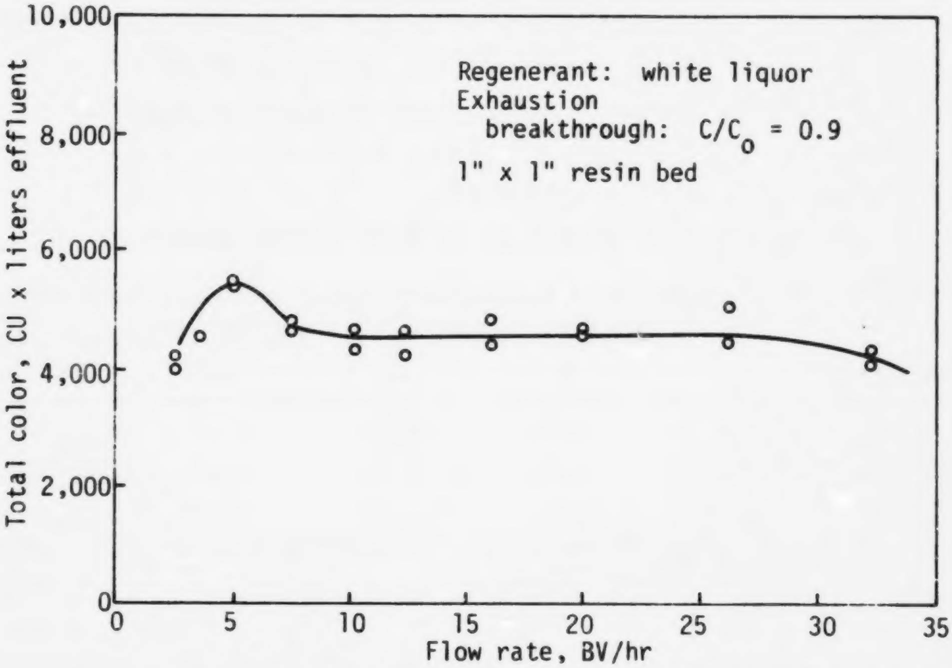

FIGURE 58. EFFECT OF FLOW RATE UPON REGENERATION EFFICIENCY OF A-6 RESIN

The optimum flow rate in Duolite S-37 was approximately 25 BV/hr as shown in Figure 59. No anomalies were found in these runs. Efficiency decreased below 20 BV/hr and above 30 BV/hr.

As shown in Figure 60, the best flow rate tested for Amberlite IRA-68 was 10 BV/hr. From the shape of the curve it seems likely that higher efficiencies might be found at still lower rates. The low concentrations and the low flow rates combine to require a long time for efficient regeneration.

Regeneration level. The optimum quantity of regenerant can be only approximately determined from these short-column experiments. The regenerant does not pass through the column in plug flow. Instead, there is dispersion of the front and tailing of the end. Shallow resin beds give little indication of this action. However, a first approximation of the optimum quantity of regenerant can be gleaned by estimating the point where a plateau begins in the elution history shown in Figures 53, 55, and 57. These estimated points are given in Table 20, and the amount of color eluted is given in Table 21.

TABLE 20

ESTIMATED OPTIMUM QUANTITIES OF WHITE LIQUOR REGENERANT

	Quantity Regenerant, me NaOH/ml resin				
Resin	3N	2N	1N	0.5N	0.25N
A-6	24.6	16.5	10.2	--	--
S-37	17.2	14.5	12.6	--	3.8
IRA-68	18.3	14.5	12.8	12.0	7.6

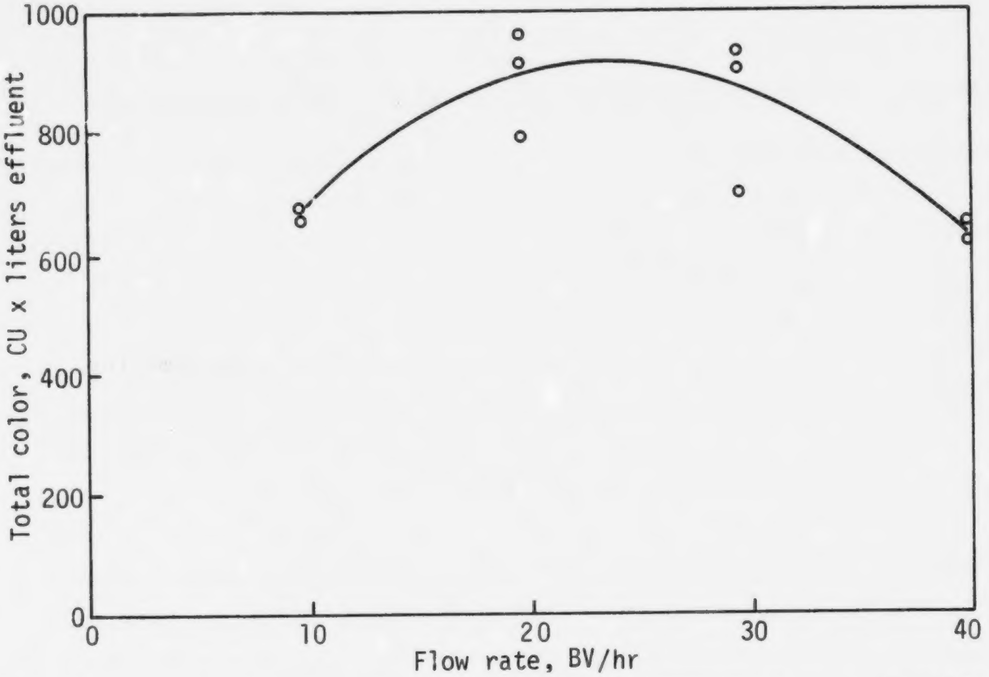

FIGURE 59. EFFECT OF FLOW RATE ON REGENERATION EFFICIENCY OF S-37 RESIN

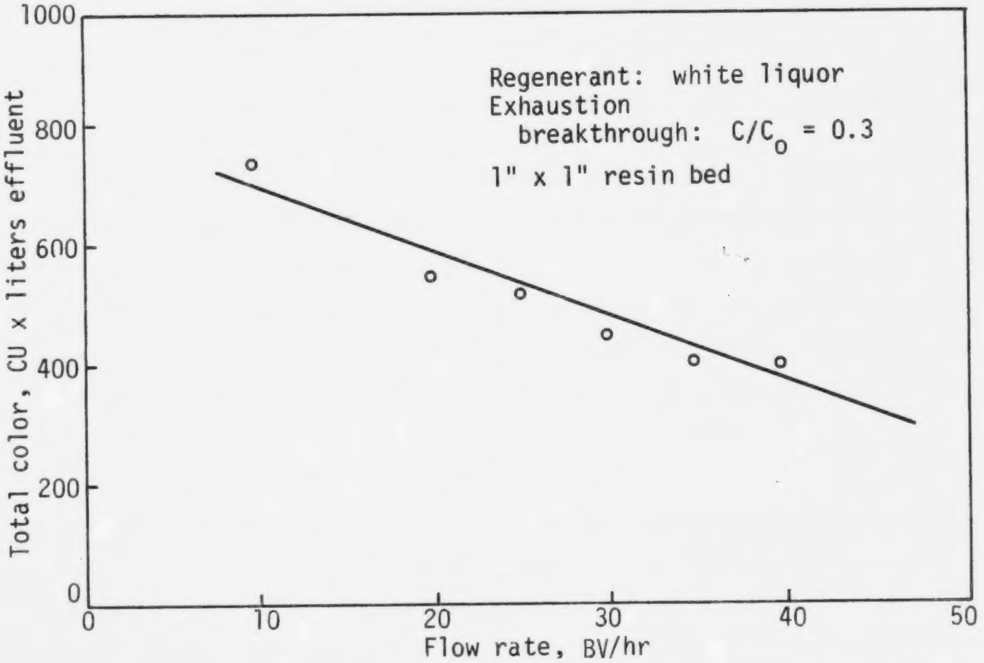

FIGURE 60. EFFECT OF FLOW RATE ON REGENERATION EFFICIENCY OF IRA-68 RESIN

TABLE 21

COLOR ELUTED AT OPTIMUM QUANTITIES OF WHITE LIQUOR REGENERANT

	Total color eluted, CU-liters/me NaOH				
Resin	3N	2N	1N	0.5N	0.25N
A-6	15.9	18.6	27.5	--	--
S-37	3.8	4.4	5.4	--	7.5
IRA-68	0.3	0.7	1.3	1.9	3.3

Comparison of Resins in Single Runs

Comparing one resin with another on the basis of a series of single runs can be quite misleading. Conclusive comparisons can only be made with cyclic runs in which the resins reach cyclic stability. Irreversible sorption, blinding, and chemical and physical degradation are factors which cannot be judged from single runs.

Cyclic Runs

During the cyclical runs, the capacity of resins regenerated with white liquor continued to decline. Rejuvenation with hydrochloric acid fully restored the resin, but the procedure would have to be repeated about every 10th cycle, which in a prototype would mean a daily rejuvenation procedure. Hence, other regenerants were tried, some in single runs, others in a few cyclical runs, and still others in a lengthy series of cyclical runs.

White liquor regeneration. As shown in Figures 61 and 62 both Duolite A-6 and S-37 gradually lost capacity to sorb color from bleach waste when regenerated at 16 BV/hr with white liquor. After 9 cycles of sorption runs, the original capacity of the resin was reduced to less than 50 percent. Neither rejuvenation with 4 BV of methanol nor with

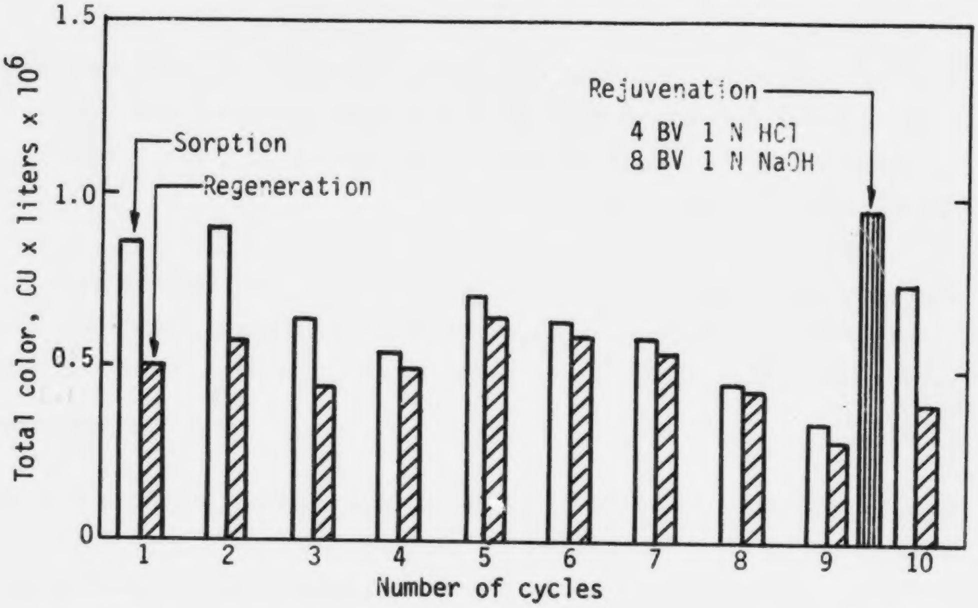

FIGURE 61. COLOR REMOVAL BY DUOLITE A-6 RESIN REGENERATED WITH WHITE LIQUOR

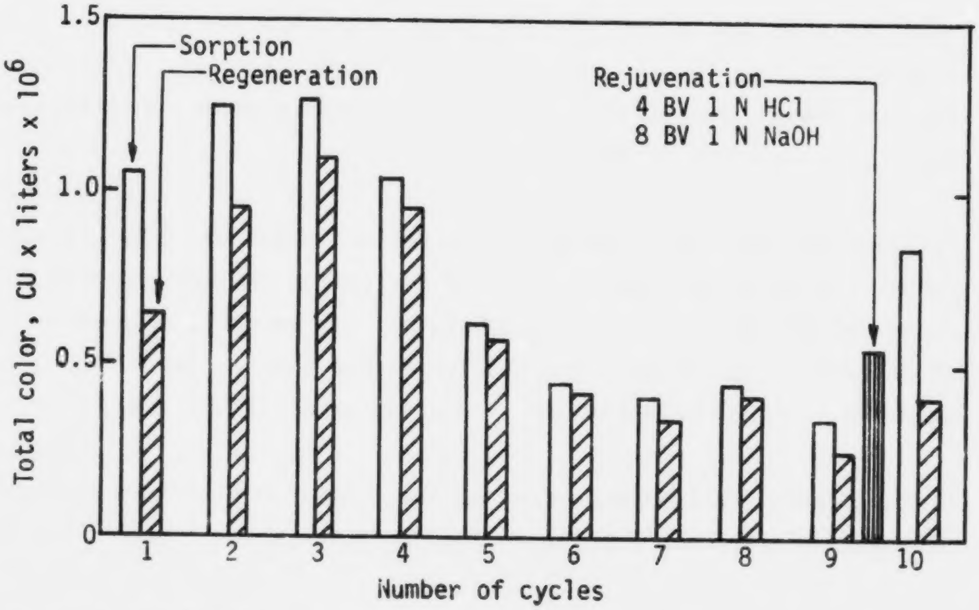

FIGURE 62. COLOR REMOVAL BY DUOLITE S-37 RESIN REGENERATED WITH WHITE LIQUOR

4 BV of 10 percent NaCl had much affect. However, rejuvenation with 4 BV of 1 N HCl followed by 8 BV of 1 N NaOH restored both resins to their original, virgin appearance and nearly to their original capacity for the sorption of color.

The loss of capacity appeared to be associated with some sulfide precipitation as well as precipitation of carbonates. When the resins were treated with hydrochloric acid, great quantities of CO_2 gas were evolved.

Caustic regeneration. When the resins were regenerated with 1 N NaOH, there was little or no decline in the sorption capacity of Duolite A-6 after the first cycle. As Figure 63 shows, the sustained sorption capacity was approximately 80 percent of the virgin sorptive capacity.

Duolite S-37 resin exhibited somewhat anomalous behavior. It's sorptive capacity, as shown in Figure 64, was greater in the second cycle than for the virgin resin. After the third cycle its capacity began to rise slowly. At the 9th cycle, its capacity decreased abruptly to less than 60 percent of its virgin capacity. Although the two resins (Duolite A-6 and S-37) are nearly equal, Duolite A-6 was more consistent in performance.

Sorption and elution breakthrough curves for color and total organic carbon are shown in Figures 65 to 68 for one of the last runs in a series after cyclic equilibrium was established. In general, approximately 30 percent of the color broke through almost immediately with a gradual increase of color breakthrough to the end point of the run.

Little organic carbon was sorbed by the resin. Duolite A-6 was considerably better than Duolite S-37 in this respect.

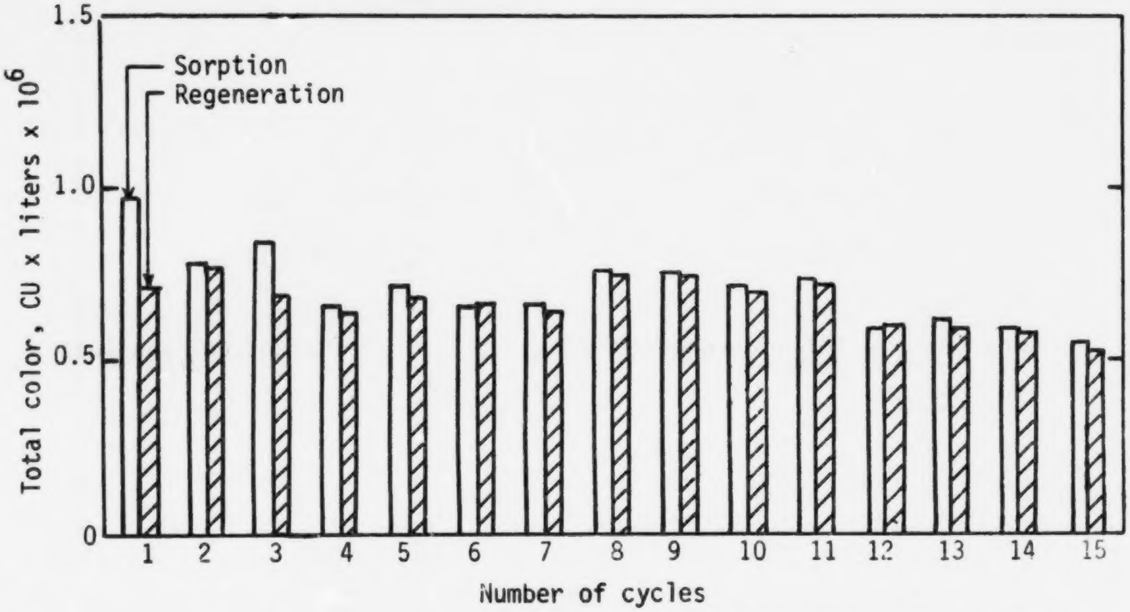

FIGURE 63. COLOR REMOVAL BY DUOLITE A-6 RESIN REGENERATED WITH CAUSTIC

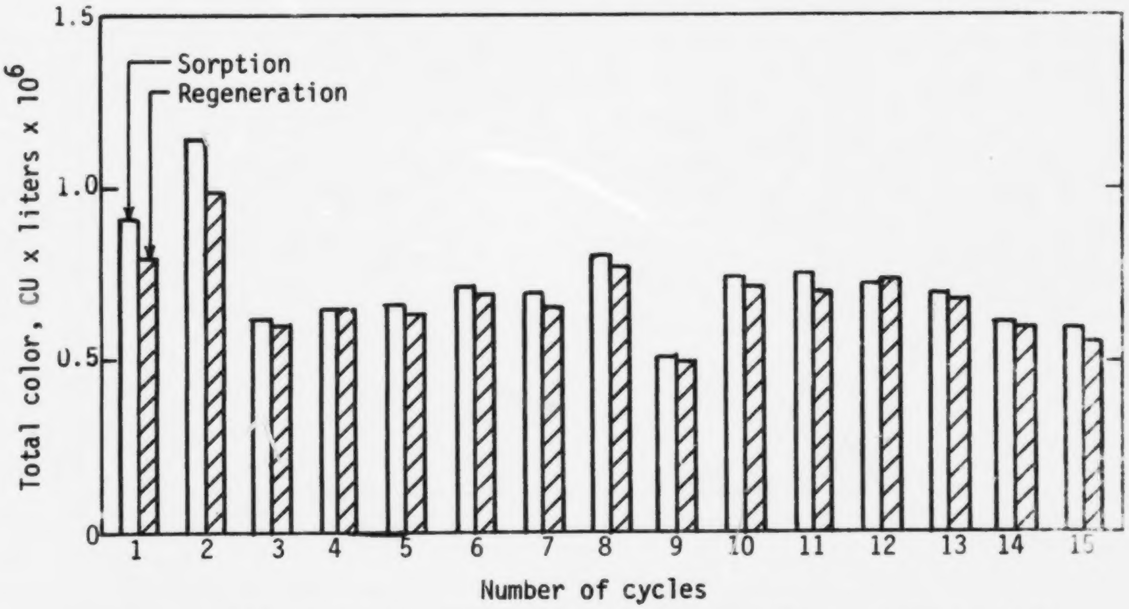

FIGURE 64. COLOR REMOVAL BY DUOLITE S-37 RESIN REGENERATED WITH CAUSTIC

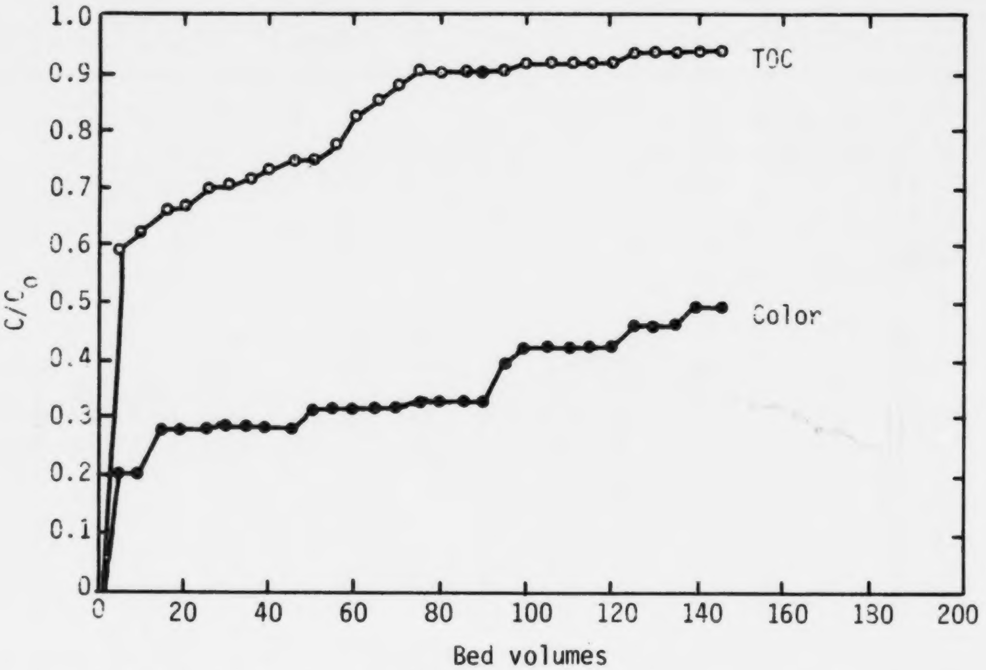

FIGURE 65. COLOR AND TOC BREAKTHROUGH IN 13TH CYCLIC RUN. DUOLITE A-6 RESIN. CAUSTIC REGENERATION

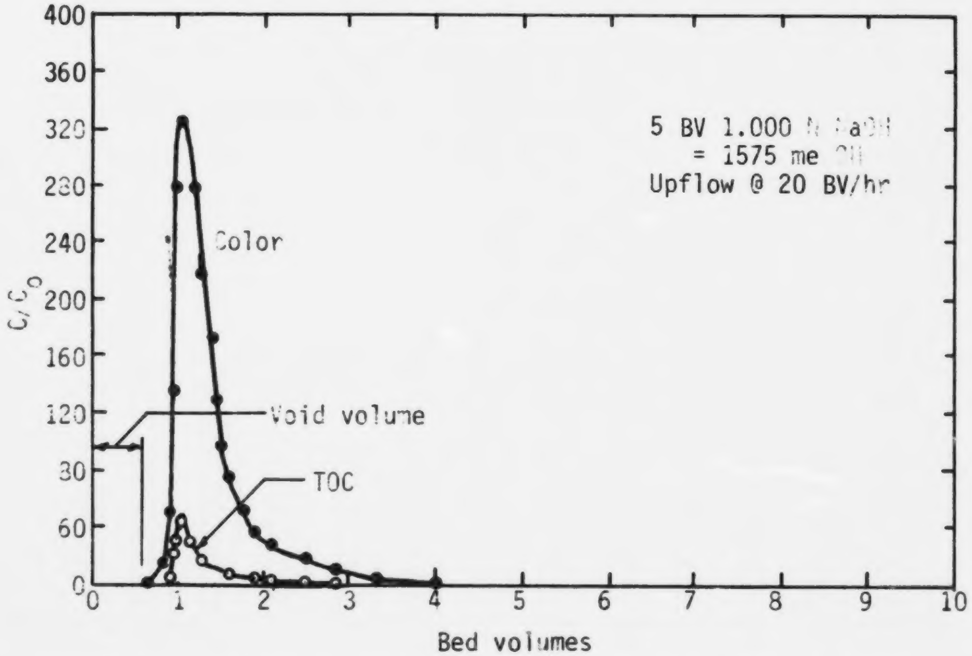

FIGURE 66. ELUTION OF COLOR AND TOC IN COUNTERCURRENT CAUSTIC REGENERATION OF DUOLITE A-6 RESIN IN 13TH CYCLIC RUN

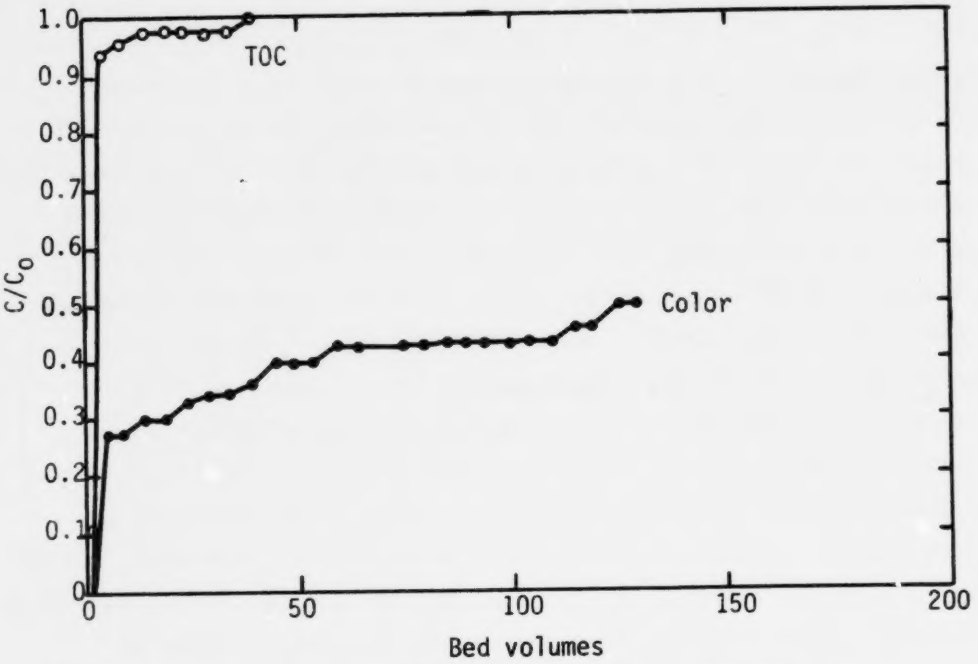

FIGURE 67. COLOR AND TOC BREAKTHROUGH IN 14TH CYCLIC RUN. DUOLITE S-37 RESIN. CAUSTIC REGENERATION

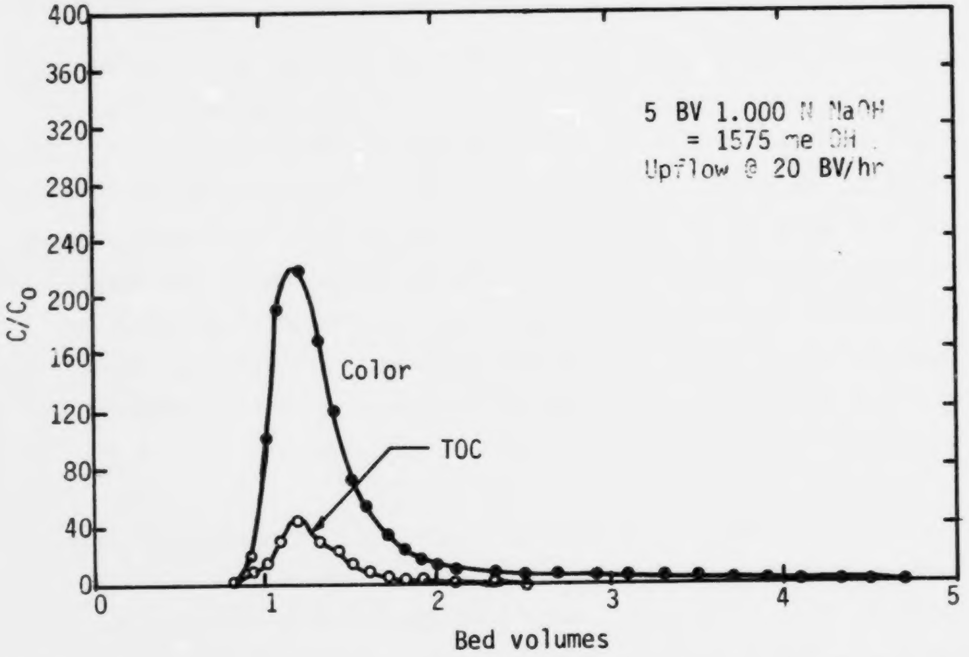

FIGURE 68. ELUTION OF COLOR AND TOC IN COUNTERCURRENT CAUSTIC REGENERATION OF DUOLITE S-37 RESIN IN 14TH CYCLIC RUN

Amberlite XAD-8 and weak wash regeneration. News of a new resin, Amberlite XAD-8, was received late in 1971 after the program on color sorbency was completed. A decision was made not to interrupt desalination runs with more color sorbency runs, and nothing was done with XAD-8 until the life cycling runs were begun. The results of the few preliminary tests were poor, so little interest in XAD-8 was aroused. In discussing these results, Button (1972) stated very low pH of the feed was necessary for good operation of this resin, and furthermore regenerants containing one normal equivalent NaOH were too strong. Button reported excellent results on many artificial bleach plant effluents (blends of chlorine and caustic wastes) in which the pH was always less than 3, and since, in his experience, the pH of bleach plant liquors was invariably low, the need for low pH was not mentioned in the literature. The experiments described herein follow the recommendations of Rohm and Haas literature (1971). No attempt was made to optimize operating conditions.

Raw artificial ditch waste (pH 6.5) was acidified to pH 2.2 by adding 0.1 percent H_2SO_4 by weight. Corrected to pH 7.6, the intensity of color was 2800 CU. Figure 69 shows the fourth run in a series in which the XAD-8 was regenerated countercurrently (as shown in Figure 70) with 2 BV of weak wash at a flow rate of 1 BV/hr upflow. The sharp drop in color at the beginning of the run in Figure 69 is due to the displacement of the regenerant by the ditch waste, and the low color at about 3 BV shows the resin is capable of sorbing nearly all kinds of color bodies. It suggests that a series of columns (as in Progressive Mode) would be capable of producing a colorless effluent.

These results are significant because they indicate resins can indeed be tailored for optimum operation. If the operation of such resins can be integrated sufficiently well into the pulping process, the use of resinous sorbents for the color reduction of raw wastes might be the most satisfactory and economical of all methods developed to date.

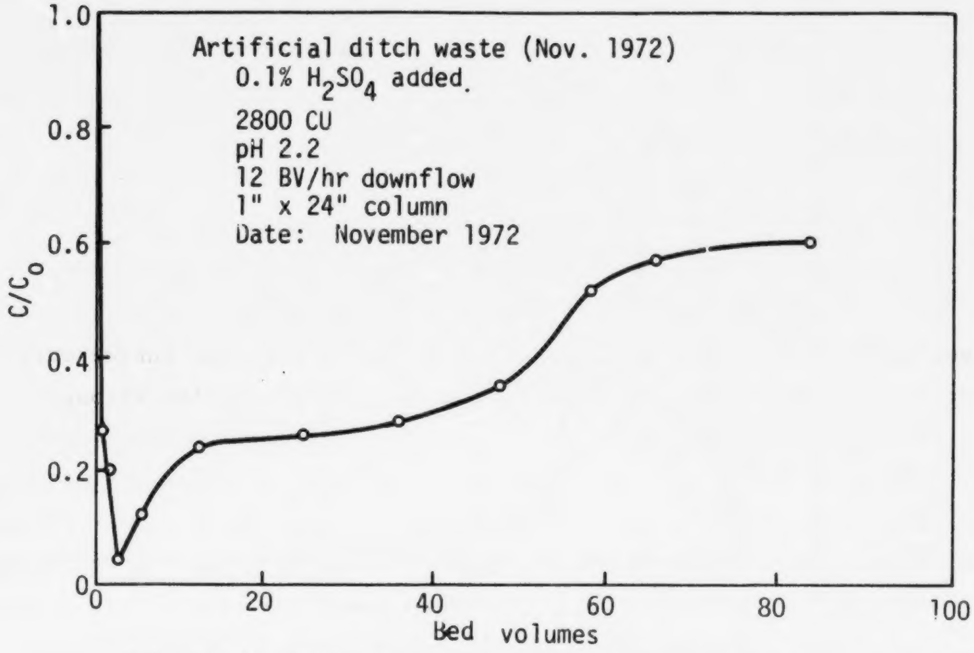

FIGURE 69. FOURTH RUN OF COLOR SORPTION FROM RAW DITCH WASTE BY XAD-8.

Although little attempt was made to optimize the regeneration conditions shown in Figure 70, a few runs proved concentrated bases such as white liquor and 1 N NaOH were not as good as weak wash. Attempts to regenerate at high flow rates were unsuccessful. If no improvement in these low flow rates can be made, the amount of resin required to treat the bleach waste of the Hoerner Waldorf Mill would have to be large.

Carbon. Sorption of color by carbon as shown in Figure 71 was far superior to the results obtained for carbon in any of the previous experiments. Previously, virgin resins were always competitive with or superior to carbon for the sorption of color.

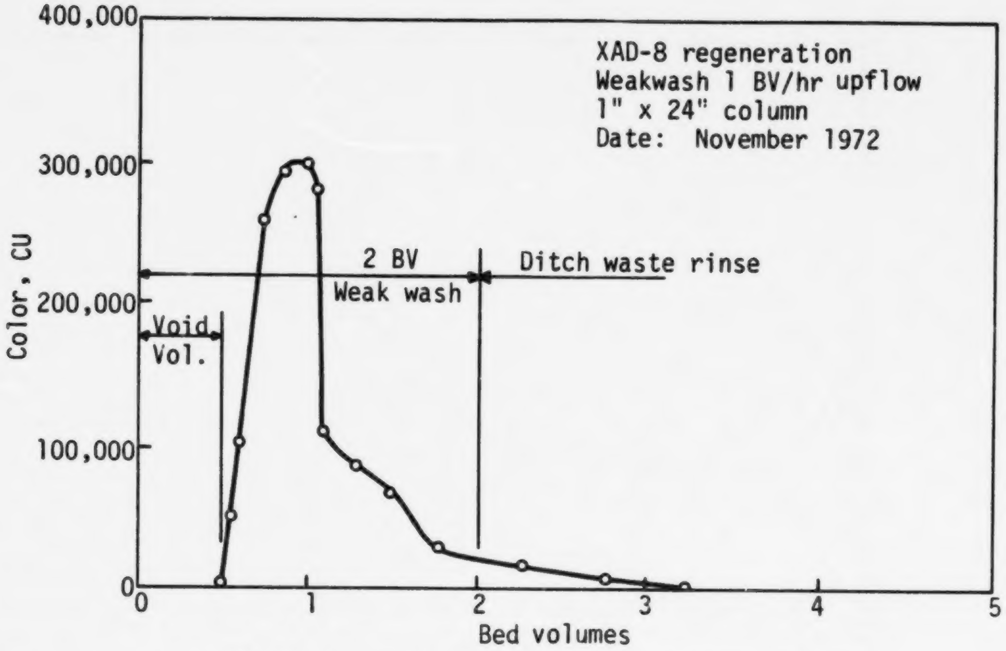

FIGURE 70. REGENERATION OF XAD-8 WITH WEAK WASH

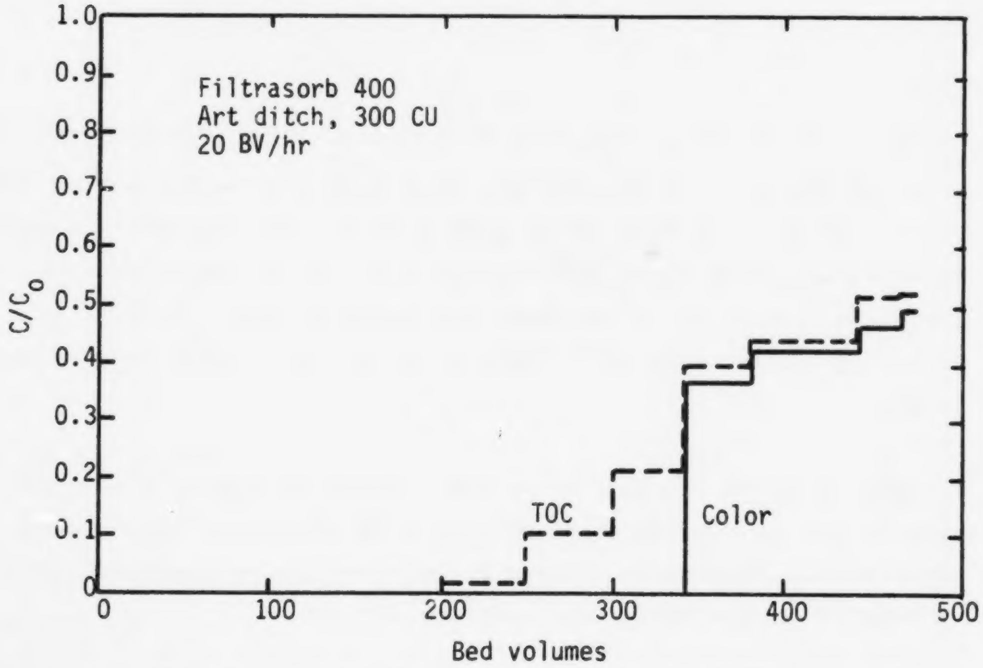

FIGURE 71. COLOR AND TOC BREAKTHROUGH IN VIRGIN FILTRASORB 400 CARBON

DESALINATION

The first run on both cation and anion resins in both exhaustion and regeneration were carried far beyond initial breakthroughs to help assess a satisfactory breakthrough limitation for subsequent cyclic runs.

Virgin Resins

Cation exchange. Breakthrough histories for cations and for the parameters pH, TOC, and specific conductivity are shown in Figure 72 for the first run of a series. There was no effect on color, so color is not shown. As would be expected, sodium is the first ion to break through, and a corresponding sharp decrease of specific conductivity heralds this event. Specific conductivity is an easy parameter to monitor for the control of this kind of ion exchange. At this level of regeneration (11.4 lb HCl/cu ft resin) about 60 BV of feed pass through the column before breakthrough. About 140 BV of feed pass through the column before calcium begins to appear. The relative amounts of sodium and calcium in the effluent can be controlled by altering the end point.

Breakthrough curves for regeneration (with 5 BV of 0.915 N H_2SO_4) of resin exhausted only to 35 percent breakthrough of Na are shown in Figure 73. The large surplus of H ions as compared to Na plus Ca ions show that the regeneration efficiency is low -- approximately 22 percent. The regeneration efficiency can be increased in a number of ways: (1) by using less regenerant (starvation regeneration), (2) by the addition of a weak acid resin to the column which makes a "Duo-Cat" column, and (3) by use of a more sophisticated ion exchange system such as: 2-stage cation-anion-cation-anion columns, a Progressive Mode system, or by continuous countercurrent ion exchange such as the Graver

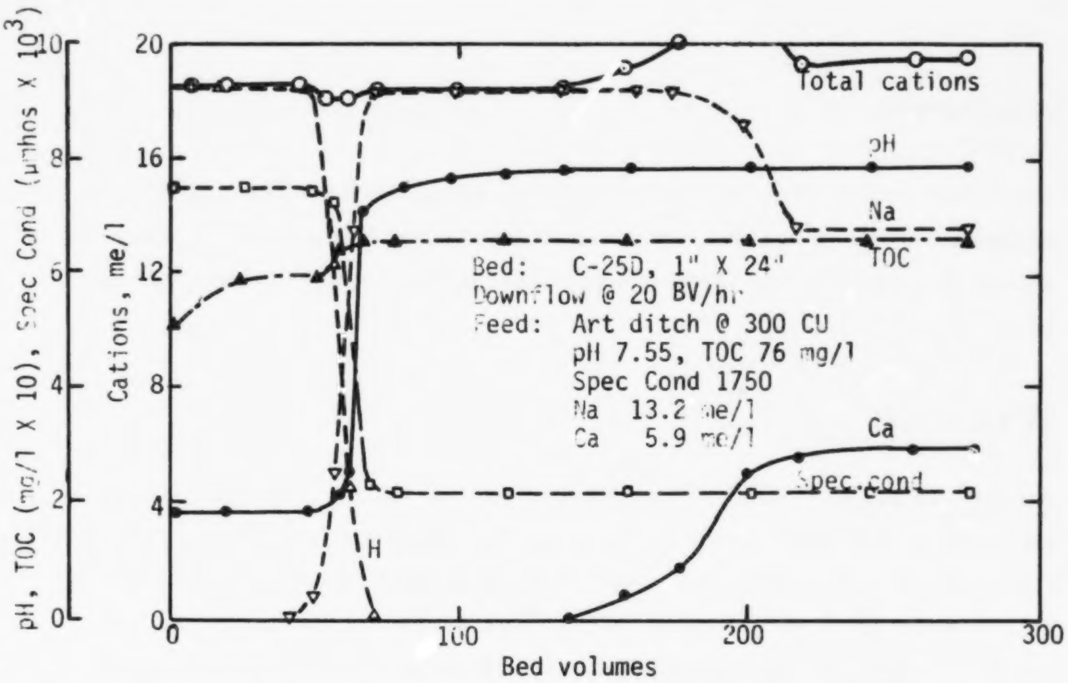

FIGURE 72. EXHAUSTION BREAKTHROUGH CURVES OF IONS AND PARAMETERS OF PERFORMANCE IN CATION EXCHANGE

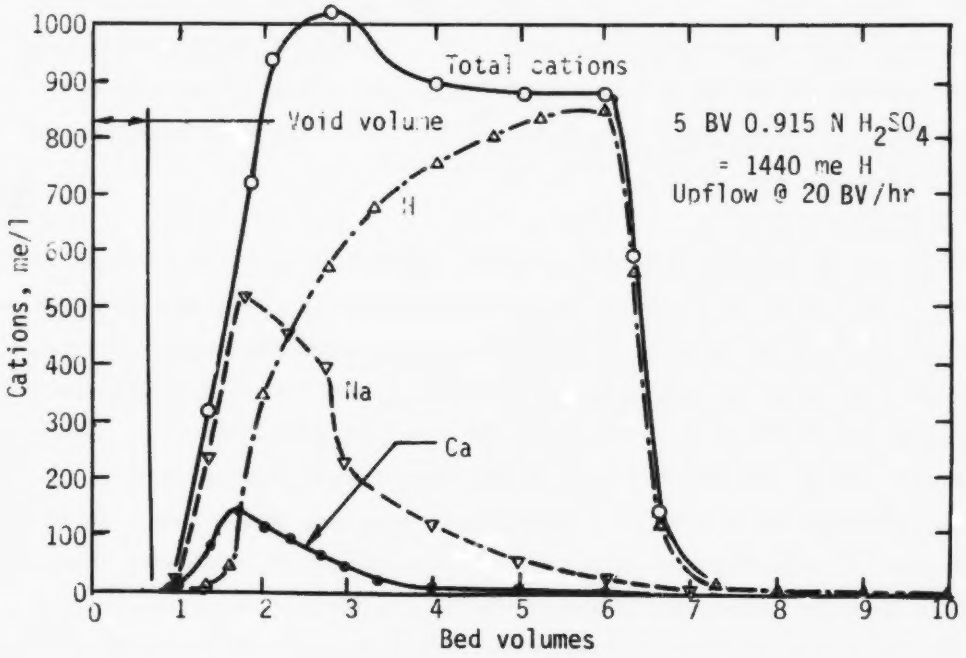

FIGURE 73. REGENERATION BREAKTHROUGH CURVES IN CATION EXCHANGE

CCIX system or the Chem-Seps continuous countercurrent ion exchange system.

The feed for the first cation run was artificial ditch waste pretreated by massive lime precipitation and two-stage recarbonation to a pH of 7.6. The concentration of ions are shown in Table 22.

Anion exchange. Analysis of the feed to the anion column, the decarbonated cation effluent, is shown in Table 23. Discrepencies between analyses of cation and anion feeds are the result of treatment of different batches of bleach plant waste. Treatment by massive lime precipitation results in a fluctuation of ionic concentrations. These fluctuations are likely to be typical of those that would be experienced in the operation of a prototype and hence no attempt has been made to reduce the normal fluctuations.

Figure 74 shows the complete breakthrough curve for the chloride ion. No other anions appeared in more than trace quantities in the effluent. The run was halted at this point because the other ions were present in such small amounts that equilibrium of effluent with feed would require inordinate volumes of liquor. Effluent color never reached 40 percent of the influent color. The control of the anion exchange column could be achieved by monitoring conductivity, instantaneous pH, or the pH of the total mixed effluent. As the pH of process streams is important, control of the column by monitoring the pH of the mixed effluent is probably the most desirable means.

For the study of regeneration, it was desirable to begin with a resin partially exhausted to approximate the condition to be found in cyclic operation. Consequently, columns of Duolite A-6 resin were exhausted to a chloride breakthrough of approximately 35 percent or 4.5 me/l. This corresponds to a througnput of 80 to 90 BV and a mixed liquor pH of approximately 6.8. Such a mixed liquor pH is somewhat too low

TABLE 22

TYPICAL CONCENTRATION OF IONS IN CATION FEED

Cation	Concentration me/l		Anion	Concentration me/l	
	Run #2	Run #3		Run #2	Run #3
K	tr	tr	HCO_3	5.3	4.3
Na	18.0	13.2	Cl	17.2	12.9
Ca	6.6	5.9	NO_3	tr	tr
Mg	tr	tr	SO_4	0.6	1.4
			S	tr	tr
Sum	24.6	19.1		23.1	18.6

TABLE 23

TYPICAL CONCENTRATION OF IONS IN ANION FEED
Effluent from 2-inch column

Cation	Concentration me/l	Anion	Concentration me/l
H	9.9	H_2CO_3	0.1
Na	3.1	Cl	13.2
Ca	0.0	NO_3	tr
Mg	0.0	SO_4	0.1
	13.0	S	tr
		Error = 3.0%	13.4
pH = 2.0			

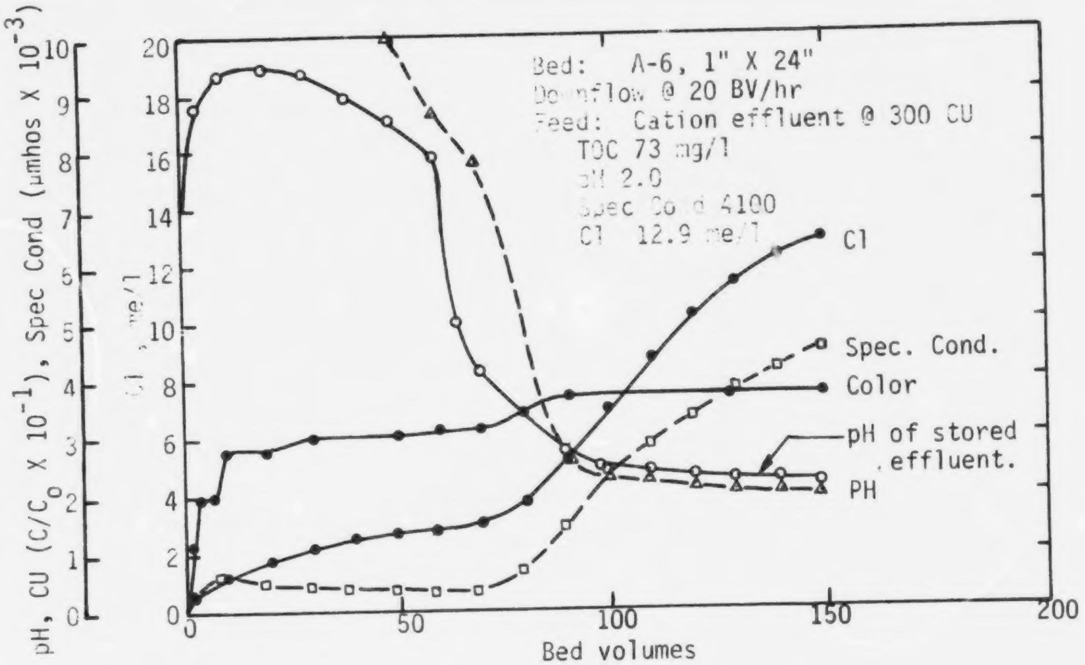

FIGURE 74. EXHAUSTION BREAKTHROUGH CURVES OF CHLORIDE ION AND PARAMETERS OF PERFORMANCE IN ANION EXCHANGE

for process water in the plant, but examination of Figure 74 shows the pH of the mixed liquor to be changing very rapidly with small changes of throughput volume. In a prototype, it would be easy to produce any desired pH of the mixed effluent.

Lime slurry regeneration. Attempts to regenerate Duolite A-6 resin with 4 percent lime slurry were only partially successful. In one set of experiments, the resin was removed from the column and stirred by air for 10 minutes in one liter of a 4 percent lime slurry. The lime slurry was then drained and replaced for a second treatment. This was repeated five times as shown in Figure 75. Most of the color and the chloride ion were removed in the first treatment, but elution of chloride continued in succeeding treatments.

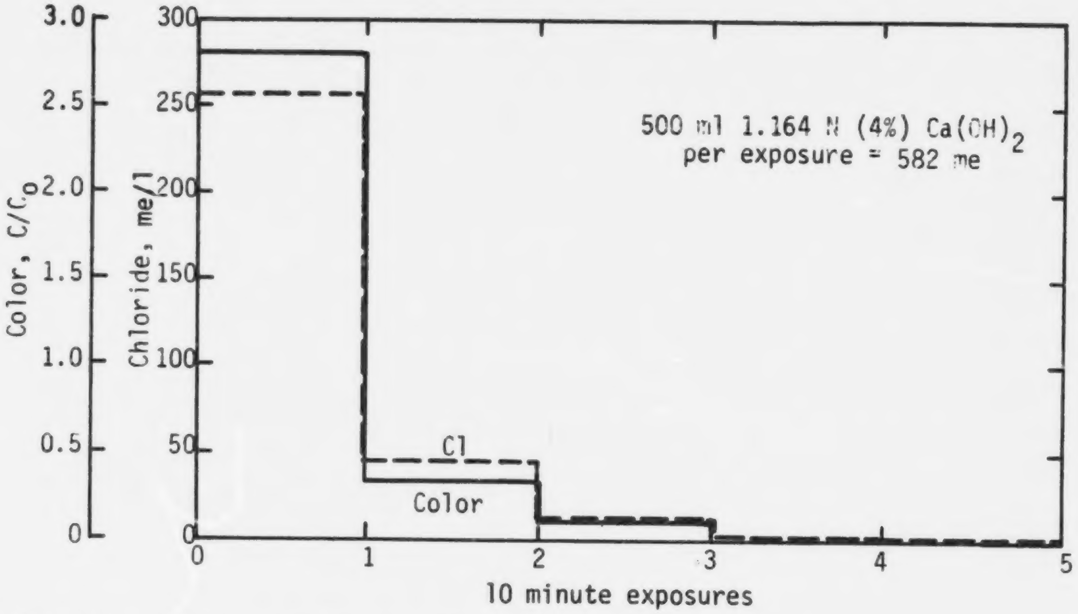

FIGURE 75. SERIAL BATCH REGENERATION OF DUOLITE A-6 RESIN WITH 4% LIME SLURRY AND AIR MIXING

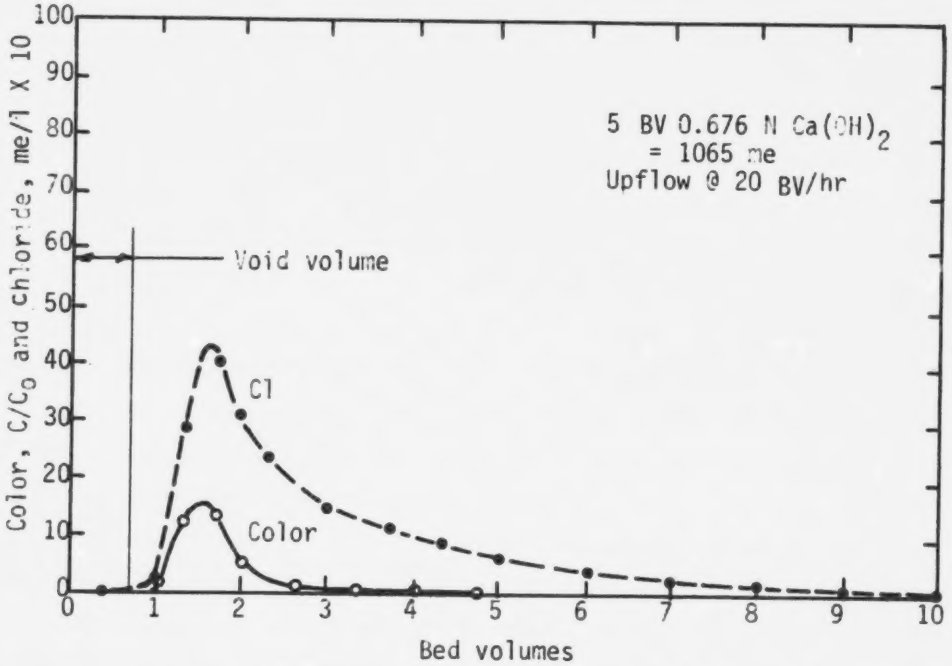

FIGURE 76. COLUMN REGENERATION OF DUOLITE A-6 RESIN WITH LIME SLURRY

The regeneration efficiency for the first treatment was 48 percent, where regeneration efficiency is defined as "milliequivalents anions eluted divided by milliequivalents of regenerant used." The efficiency of regeneration for the first two treatments was 28 percent.

Regeneration of the resin within the column by upward flow of 4 percent lime slurry at the rate of 20 BV/hr is shown in Figure 76. Using five BV of 4 percent lime slurry, the regeneration efficiency was 15 percent. The removal of color was somewhat better than the removal of chloride ion.

Ammonia regeneration. The elution of color and chloride during column regeneration of Duolite A-6 resin with ammonia is shown in Figure 77. Five BV of 4 percent ammonia (1710 me) was used at an upflow rate of 20 BV/hr. The regeneration efficiency was 12 percent. It is obvious the regeneration would have been nearly as complete with much less ammonia. Hence, it can be expected that regeneration efficiencies with ammonia could be vastly improved.

Caustic regeneration. Column regeneration with caustic (1 N NaOH) is shown in Figure 78. Five BV of 1 N NaOH was used at an upflow rate of 20 BV/hr. The overall regeneration efficiency was 19 percent.

Cyclic Runs

Sulfuric acid regeneration. Regeneration of Duolite C-25D resin with 1 N H_2SO_4 gave rise to problems with calcium sulfate precipitation. Decreasing the concentration to 3 percent H_2SO_4 (0.6 N) eliminated the problem with calcium sulfate.

The quantity of acid for optimum regeneration is shown in Figures 79 and 80. On the basis of these figures, 1.3 BV of 3 percent H_2SO_4 was chosen as the optimum volume. Superficial efficiency of regeneration is calculated as

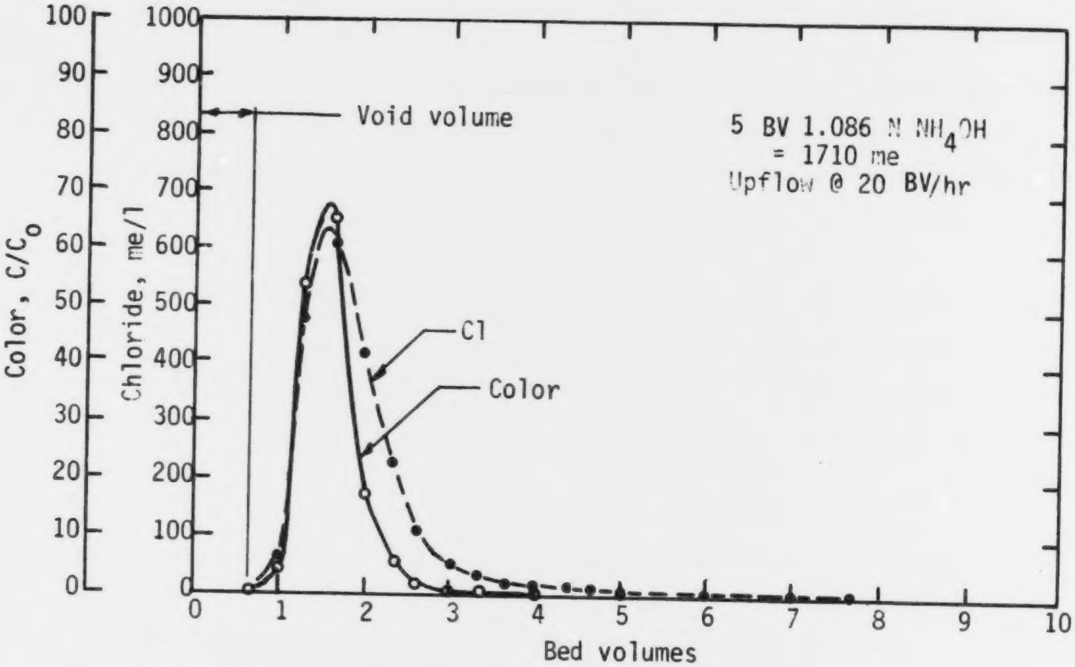

FIGURE 77. COLUMN REGENERATION OF DUOLITE A-6 RESIN WITH AMMONIA

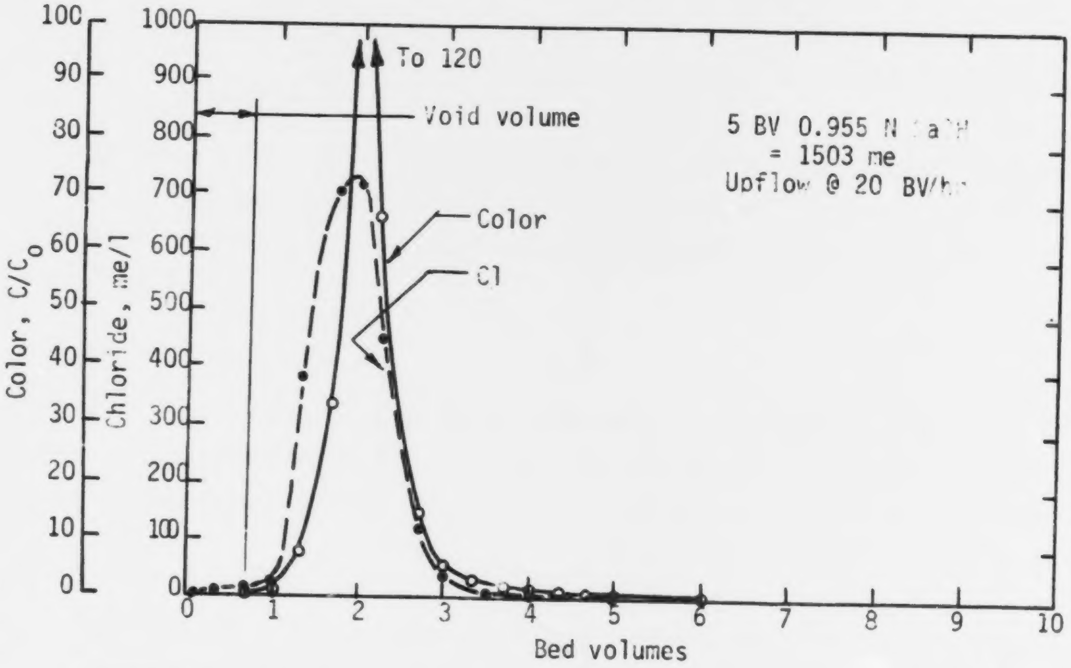

FIGURE 78. COLUMN REGENERATION OF DUOLITE A-6 RESIN WITH CAUSTIC

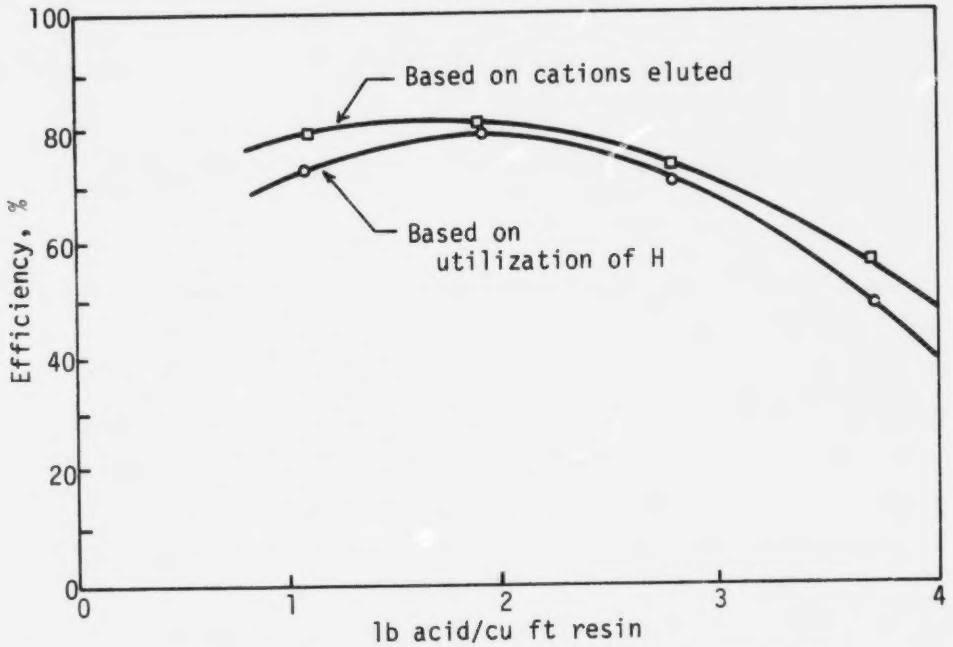

FIGURE 79. REGENERATION EFFICIENCY. C-25D RESIN

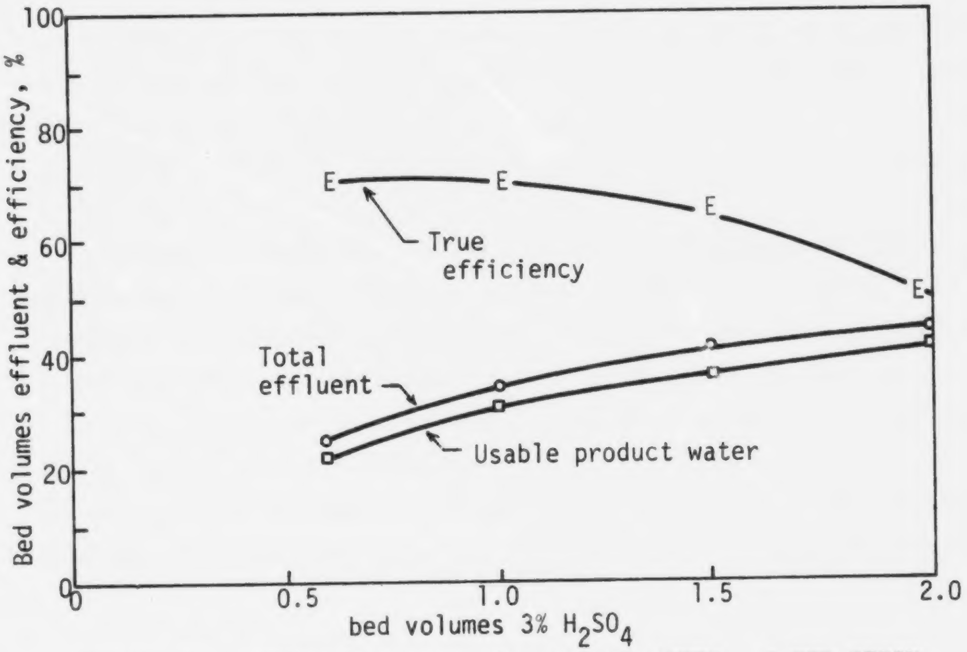

FIGURE 80. TRUE EFFICIENCY AND PRODUCT WATER. C-25D RESIN

$$\text{Superficial efficiency} = \frac{(\text{me H in})-(\text{me H out})}{(\text{me H in})} = \frac{\text{me cations eluted}}{\text{me H in}}$$

$$\text{True efficiency} = \frac{\text{me cations sorbed from net product water}}{\text{me H in}}$$

Net product water is the total throughput minus the rinse and minus the acid dilution water.

Regeneration efficiency at 1.3 BV of 3 percent H_2SO_4 was close to 71 percent. Restated, regeneration was 141 percent of stoichiometry. Although this is excellent efficiency for a strong acid resin, the efficiency can be improved in a number of ways as previously explained.

Economy of regeneration in a prototype reactor is complicated by many factors. As Figure 80 shows, an increase in the volume of acid reduces the efficiency slightly. On the other hand, it increases the quantity of useable product water. For any given size and configuration of reactor, there will be an optimum which depends not only upon these relationships but also upon the capital expenditure for the equipment, the interest rate, cost of chemicals, and sometimes practical considerations such as convenience in operation.

Caustic regeneration. The optimum amount of caustic regeneration for Duolite A-6 resin was obtained from Figures 81 and 82. The equation for the efficiency of regeneration for anion resin is the same as given for cation resin where "OH" is substituted for "H" and "anion" for "cation." The optimum bed volumes of 3 percent NaOH was also close to 1.3 BV, and for simplicity in operating both anion and cation columns, the flow rates, concentrations, volumes of regenerant, and volumes of rinse were chosen to be the same for both anion and cation resins.

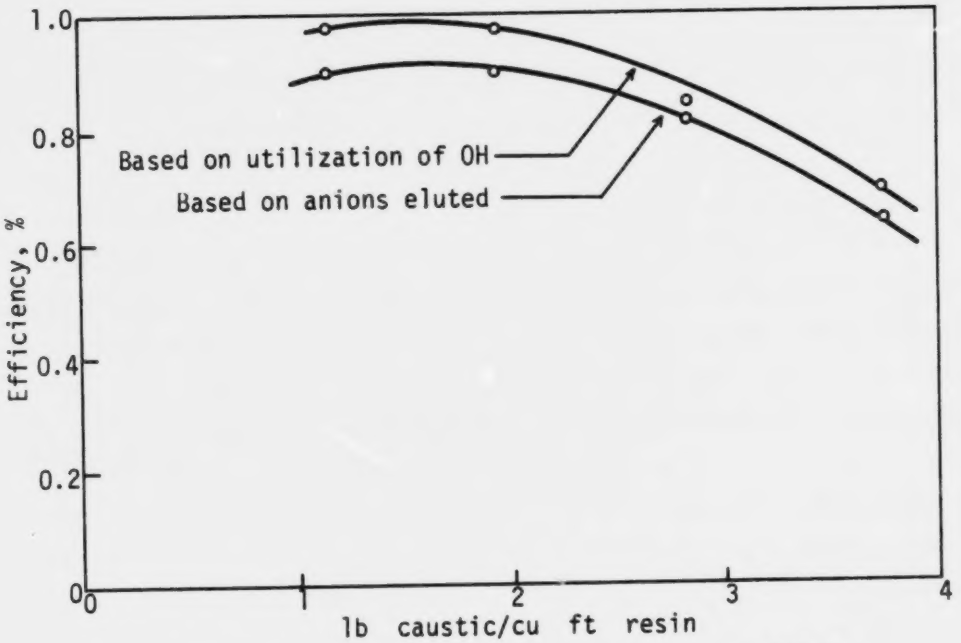

FIGURE 81. REGENERATION EFFICIENCY. A-6 RESIN

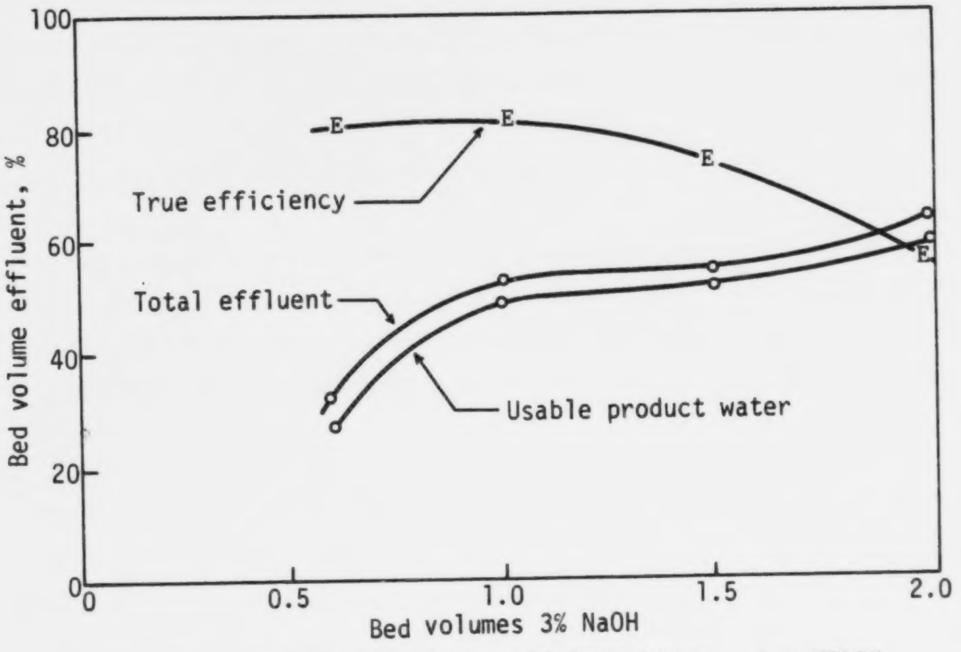

FIGURE 82. TRUE EFFICIENCY AND PRODUCT WATER. A-6 RESIN

The efficiency of 1.3 BV of 3 percent NaOH was approximately 84 percent. Restated, regeneration was 119 percent of stoichiometry.

Cation exchange. The product volume of the cation exchange column decreased during the first three cycles as shown in Figure 83 and then remained constant at 33 BV at 35 percent Na breakthrough. Because Figure 84 shows the superficial efficiency of regeneration was uniformly 77 percent, it is apparent some cations were irreversibly (at this regeneration level) sorbed during the first three cycles.

Anion exchange. Figure 85 shows the production volume in anion exchange remained constant at 55 BV per cycle at 35 percent chloride breakthrough. As shown by Figure 86, the superficial regeneration efficiency remained reasonably steady at about 84 percent.

High temperature operation. A series of runs at the temperature of the caustic extract in the caustic seal tank at the Hoerner Waldorf Mill resulted in a significant impairment in product volume and a slight decrease in regeneration efficiency as shown in Figures 87 and 88 respectively. Hence, for these resins at least, there would be a disadvantage in ion exchange of hot liquor as compared with cold liquor.

As with cation exchange, elevated temperatures did not improve the performance of the anion exchanger. Figure 89 shows the production volume increased somewhat but was more erratic. The efficiency decreased as shown in Figure 90. Hence, there was an increase in leakage.

Two-Stage Color Removal

Color leakage through the cation-anion pair of columns averaged 80 CU, a concentration too great for many uses in the mill. The object of a

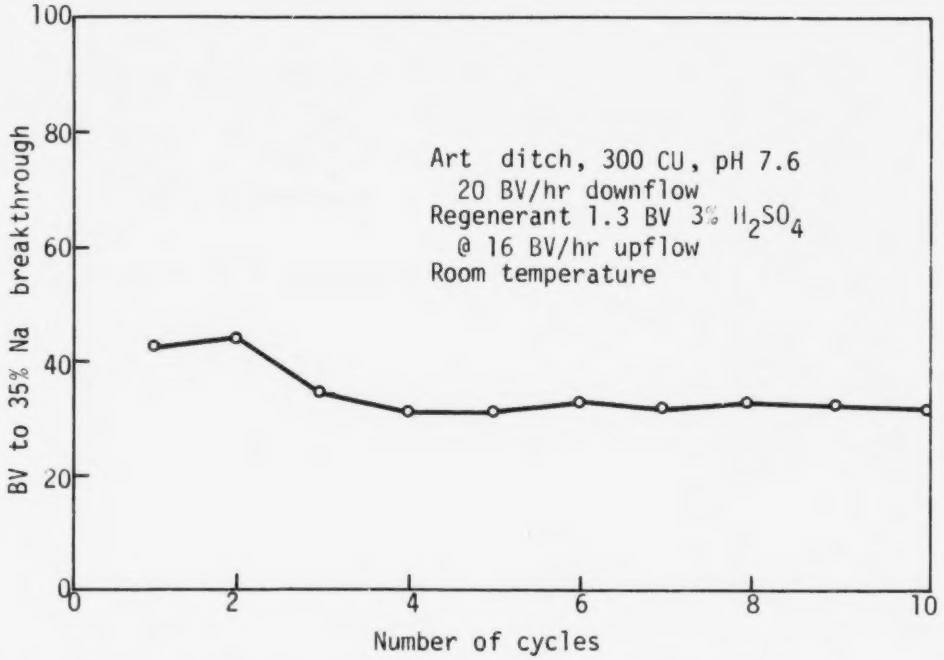

FIGURE 83. PRODUCT VOLUME IN CYCLIC CATION EXCHANGE. C-25D RESIN

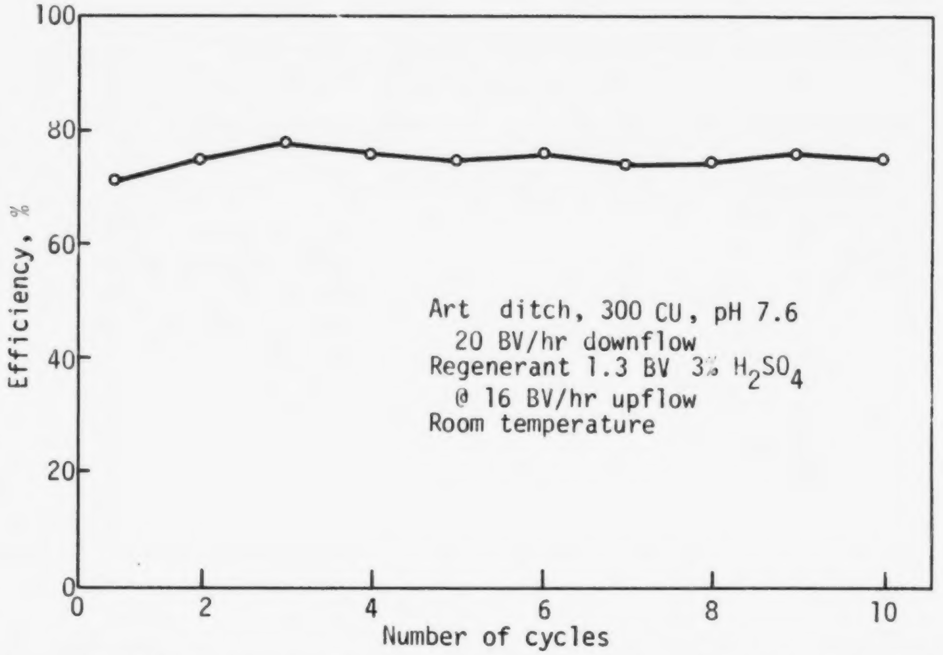

FIGURE 84. SUPERFICIAL EFFICIENCY IN CYCLIC CATION EXCHANGE. C-25D RESIN

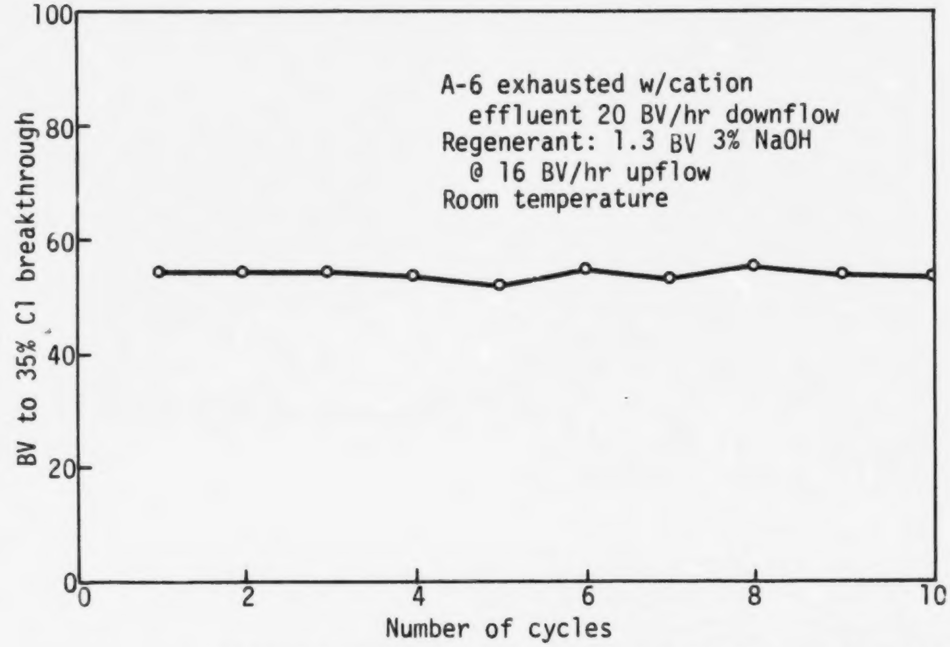

FIGURE 85. PRODUCT VOLUME IN CYCLIC ANION EXCHANGE. A-6 RESIN

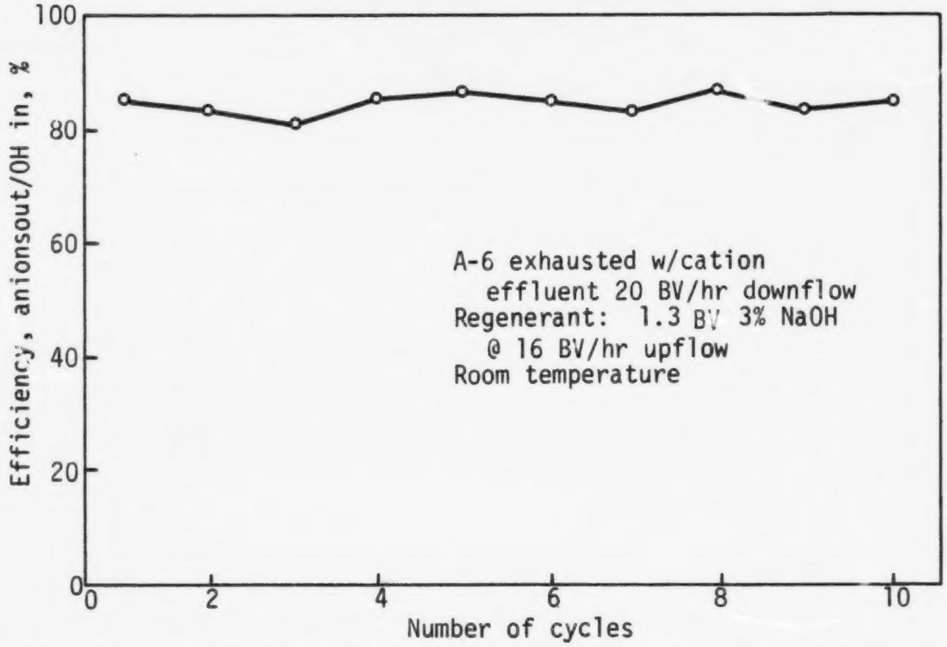

FIGURE 86. SUPERFICIAL EFFICIENCY IN CYCLIC ANION EXCHANGE. A-6 RESIN

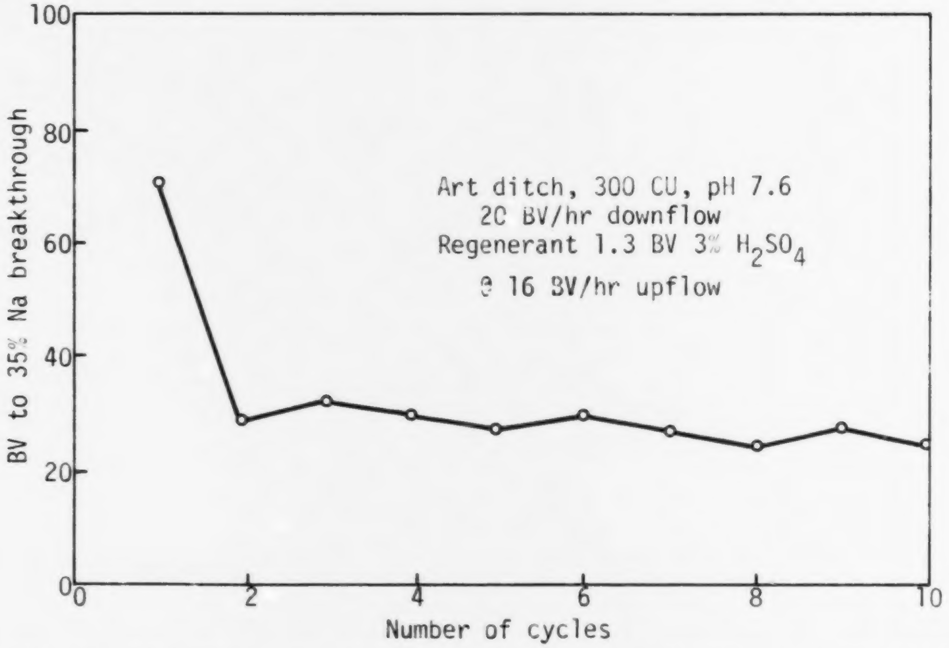

FIGURE 87. PRODUCT VOLUME AT 60°C IN CYCLIC CATION EXCHANGE. C-25D RESIN

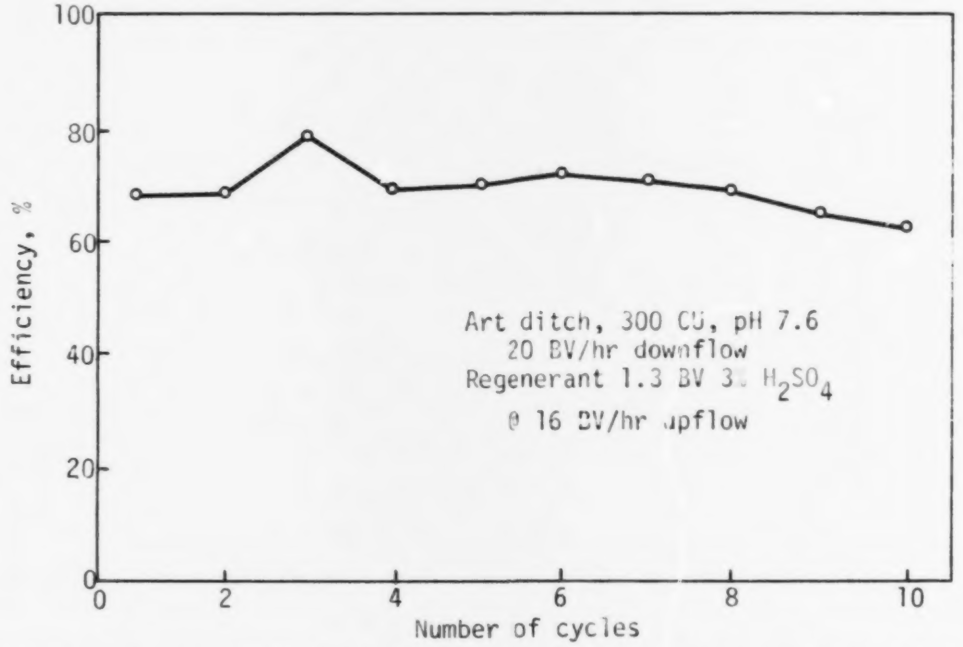

FIGURE 88. SUPERFICIAL EFFICIENCY AT 60°C IN CYCLIC CATION EXCHANGE. C-25D RESIN

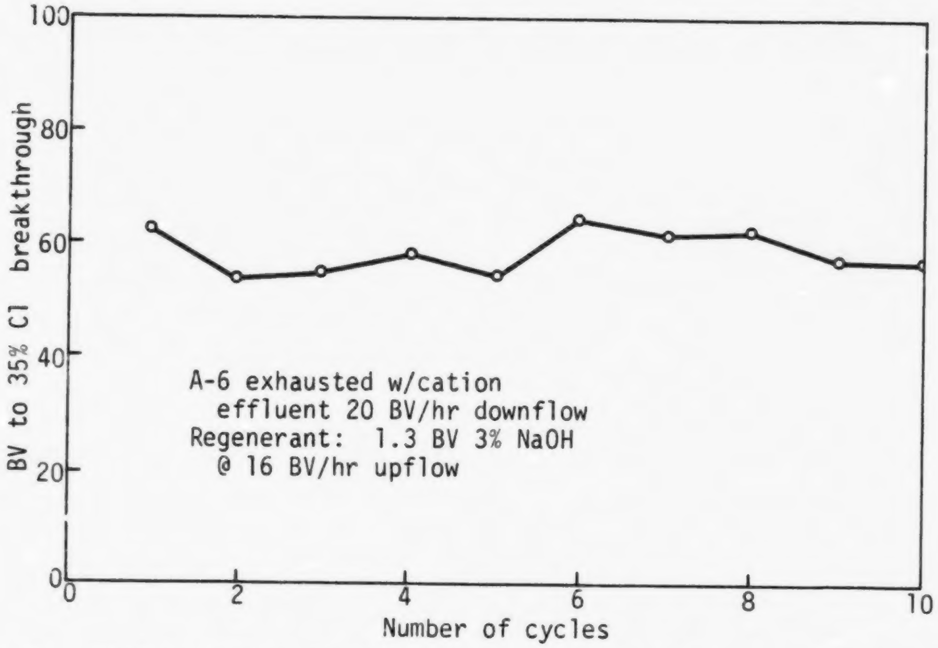

FIGURE 89. PRODUCT VOLUME AT 60°C IN CYCLIC ANION EXCHANGE. A-6 RESIN

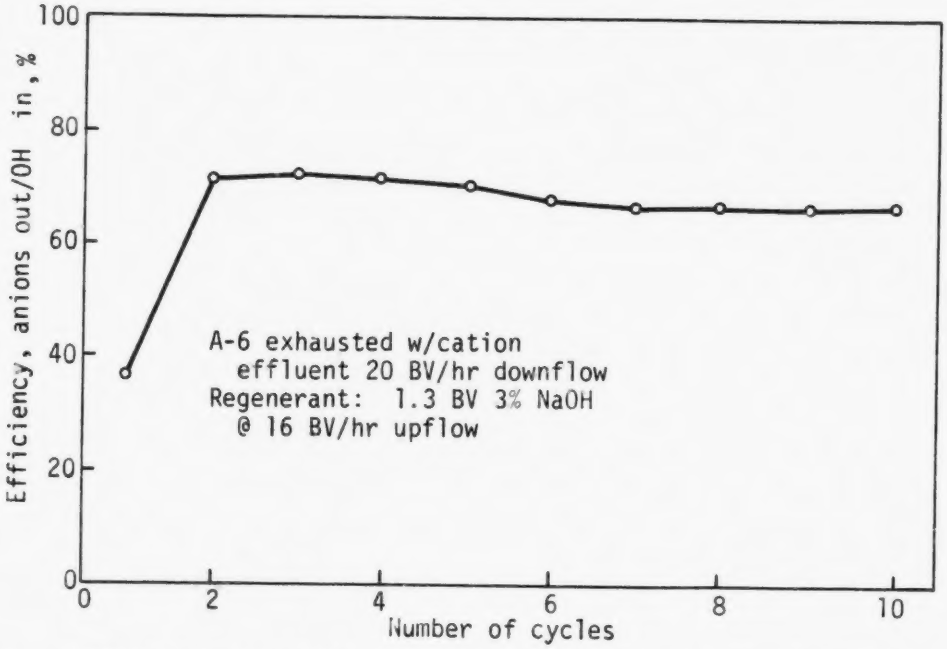

FIGURE 90. SUPERFICIAL EFFICIENCY AT 60°C IN CYCLIC ANION EXCHANGE. A-6 RESIN

second stage of treatment was to find some way to reduce the color to acceptable levels -- 8 to 10 CU.

The feed for second stage treatment was the mixed effluent from the anion column operated to a breakthrough of 35 percent of the chloride ion which resulted in a mixed liquor pH of about 6.8. In one run, the feed was acidified to a pH of 2.4 and in another run the feed was pretreated by putting it through a second cation resin column which reduced the pH to 2.15, so essentially this run was two-stage ion exchange. The conditions for seven of the eight runs are given in Table 24, and the breakthrough curves are shown in Figure 91.

A second column of used regenerated 16 x 50 mesh Duolite A-6 resin was ineffective, but fine (40 x 80 mesh) virgin A-6 was very effective. All other sorbents including Duolite A-7 and S-30 resins and even two carbons were only moderately effective. However, second stage desalination was very effective indeed. Neither color nor anion breakthrough occurred in 250 bed volumes. The success of two-stage desalination suggests a modification of the Progressive Mode system to permit two-stage desalination would produce very high quality water at regeneration efficiencies approaching 90 percent.

LIFE TESTS

Exchange Capacity

The exchange capacity of the resins is the most significant single test, and the results are given in Table 25. Four of the resins tested were received after the tests had begun and consequently there were essentially two time schedules.

In general, strong base resins performed poorly. None withstood 100 cycles. The performance of the strong acid resins was only a little

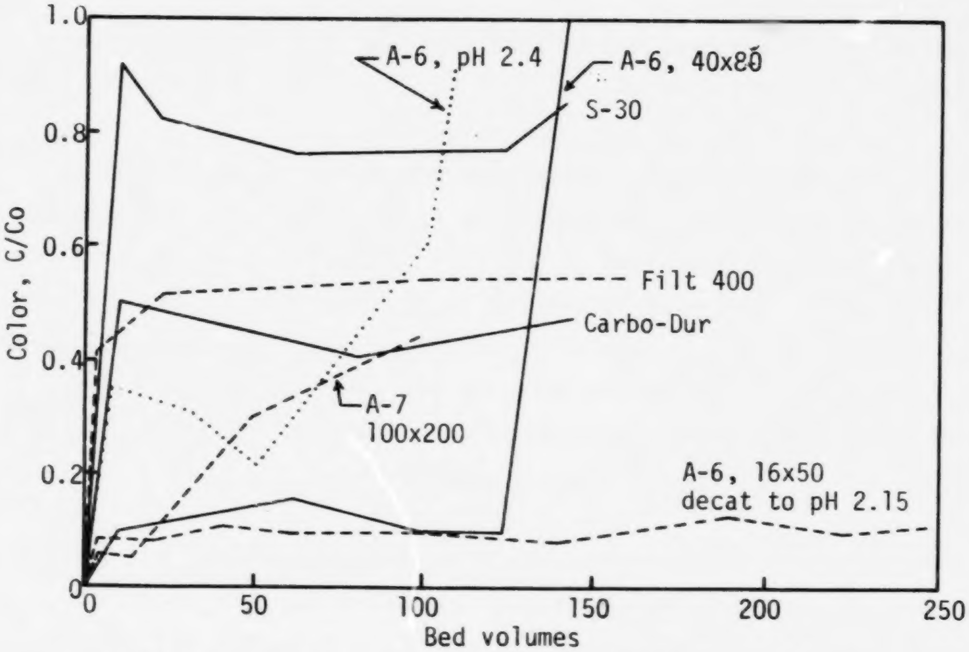

FIGURE 91. SECOND STAGE COLOR CONCENTRATION HISTORIES

TABLE 24

TWO-STAGE COLOR REMOVAL

Feed: Artificial ditch at 300 CU desalinized to pH 6.8 and 80 CU

Additional Treatment of Feed	Sorbent	Mesh	Throughput, BV	Average Color, CU
None	A-6	40 x 80	120	9
None	A-7	100 x 200	100	41
None	S-30	14 x 50	140	61
None	Filt 400	12 x 40	160	41
None	CarboDur	20 x 50	140	36
Acidify to pH 2.4	A-6	16 x 50	100	28
Decationize to pH 2.15	A-6	16 x 50	250+	8

TABLE 25
EXCHANGE CAPACITIES IN LIFE TESTS

Resin			Regen-	Exchange Capacities, me/ml								
Type	Identity	Feed	erant	0	20	80	124	255	462	637	814	989 hr
				0	8	33	52	107	189	265	334	405 cycles
Strong	C-25D	Pre	3% tech	1.6	1.6	-	1.1	0.1T				
acid	200	treated	H_2SO_4	1.9	1.7	-	1.1	1.3	-	0.1	-	0.1T
	1R 120+	Art.	"	1.7	1.7	0.1T	-	-	-	-	-	-
	HCR-W	Ditch	"	1.9	1.9	-	1.2	1.2	-	0.1	-	0.1T
Weak	IRC-84	"	"	3.8	4.0	-	3.4	3.5	-	3.5	-	3.5
acid	IRC-50	"	"	3.5	3.3	3.3	-	-	3.3	-	3.3	-
Strong	Dow 11	Cation	3% Tech	1.3	1.1	-	0.6	0.1T				
base	IRA-402	Effluent	NaOH	0.5	0.5	0.1T						
Weak	A-6	"	"	2.2	2.0	-	1.8	1.4	-	1.4	-	1.3
base	A-7	"	"	2.3	2.3	-	1.9	1.4	-	1.5	-	1.4
	IRA-68	"	"	2.1	1.7	-	1.8	1.1	-	1.0	-	0.9
	IRA-93	"	"	1.6	1.4	-	1.4	0.7	-	0.8	-	0.8
Sorbent	S-30	"	"	0.6	0.9	-	0.5	0.1T				
	S-37	"	"	2.3	2.1	-	1.8	1.7	-	1.7	-	1.6
	ES-33	"	"	0.8	0.7	-	0.7	0.1T				
	XAD-8	"	"	0.4	0.4	-	0.5	-	0.4	-	0.3	

T = Test terminated — - = no reading taken better than the performance of the strong base resins. This is a serious matter. Unless a way can be found to improve the life of the strong electrolyte resins, they cannot be used. Perhaps the strong electrolyte resins could be protected by preceeding them with weak electrolyte resins or sorbent resins, but there was no time to try such measures in this project.

The weak acid resins performed very well indeed. Neither IRC-84 nor IRC-50 lost appreciable capacity in more than 300 cycles.

Weak base resins generally performed well. But all had lost approximately half their capacity at the end of 405 cycles. The best were Duolite A-6 and A-7. Of the sorbent resins, S-37 was slightly superior to both Duolite A-6 and A-7. Because the procedures used for determining exchange capacity was a simplified and more rapid method of determination than the methods recommended in manufacturer's manuals, it is not likely that the tests are accurate to the nearest 0.1 me/ml.

Physical Characteristics

The damp weights and the minimum tamped volumes are given in Table 26. These characteristics have sometimes been used as indicators of the stability of resins. Excessive gain of moisture or excessive swelling is supposed to indicate lack of stability. But the results of Table 26 do not seem to confirm those suppositions, because resins with large changes in physical characteristics appear to retain their exchange capacities better than some other resins. The tests themselves are subjective and by their very nature liable to produce relatively large errors.

The physical appearance of resins at the beginning and end of the tests are given in Table 27. These tests are significant in showing irreversible sorption of color on the resin beads, but, more important,

TABLE 26
PHYSICAL CHARACTERISTICS OF RESINS

	Damp weight, g		Minimum Tamped vol, ml	
	Virgin	Terminated	Virgin	Terminated
Strong acid				
C-25D	21.8	20.0	27.4	26.6
Amb 200	22.3	17.6	26.8	26.0
HCR-W	22.6	21.8	27.8	27.2
IR-120+	22.7	22.7	28.0	28.2
Weak acid				
IRC-84	21.9	20.0	27.4	33.0
IRC-50	19.1	17.8	26.8	25.2
Strong base				
Dow 11	20.0	21.2	27.6	28.8
IRA-402	18.8	19.8	28.6	27.6
Weak base				
A-6	18.8	20.1	27.4	28.2
A-7	19.0	23.6	27.2	35.6
IRA-68	19.8	21.7	29.0	30.0
IRA-93	18.4	18.7	26.2	26.2
Sorbent				
S-37	19.0	22.8	27.2	34.0
S-30	17.7	20.0	27.0	31.2
ES-33	18.0	19.8	27.0	31.0
XAD-8	22.0	18.1	29.0	26.0

TABLE 27
APPEARANCE OF RESINS

Resin and type	Service life		Appearance, 30x					
			Virgin			Terminated		
	hours	cycles		cracked %	broken %		cracked %	broken %
Strong acid								
C-25D	255	107	dull tan	25	5	dull tan	30	10
Amb 200	989	405	gray-tan	0	0	gray-tan	0	10
HCR-W	989	405	clear yellow	15	0	clear amber	15	5
IR-120+	80	33	clear yellow	10	0	clear amber	10	0
Weak acid								
IRC-84	989+	405+	opaque white	0	10	amber	5	80
IRC-50	814+	334+	opaque white	0	0	opaque white	0	0
Strong base								
Dow 11	255	107	light tan	10	0	dark brown	15	5
IRA-402	80	33	yellow	25	5	dark brown	25	5
Weak base								
A-6	989+	405+	light gray-green^g			dark olive		
A-7	989+	405+	pale yellow			dark brown		
IRA-68	989+	405+	colorless	5	0	dark brown	10	0
IRA-93	989+	405+	pale tan	0	0	med brown	0	5
Sorbent								
S-37	989+	405+	tan and gray^g			dark brown		
S-30	255	107	dull red^g			reddish black		
ES-33	255	107	dark red^g			reddish black		
XAD-8	814+	334+	opaque white	0	0	opaque white	0	0

+ = Tests halted before resins failed

^{g}granular resins (cannot determine cracks or breaks) the physical stamina of the resins. The reported number of cracked or broken beads is not precise but nevertheless accurate enough to furnish insight into the physical strength and durability of the beads.

Summary

On the basis of the limited number of cyclic tests, it would appear:

(1) Weak electrolyte resins are much superior to strong electrolyte resins.

(2) Gel type strong acid resins are somewhat superior to porous strong acid resins.

(3) IRC-50 is superior to IRC-84.

(4) Duolite A-6 and A-7 are the best of the weak base resins.

(5) Duolite S-37 sorbent resin is slightly superior to Duolite A-6 and A-7 weak base resins.

(6) XAD-8 appears to be essentially unaffected.

SECTION VIII
ECONOMICS

Refinements in estimating costs of sorption of color and desalination by ion exchange are premature for several reasons. The operation of the ion exchange columns was not completely optimized. Furthermore, it seems likely that one of the more advanced ion exchange processes (such as Progressive Mode or continuous counter-current ion exchange) will be more economical than a simple cation-anion system. And a refined cost estimate should be based on experience with a large pilot plant operated for many months at a kraft mill. Life tests showed serious deterioration of all but one of the resins within little more than a month of severe operation, and as this was discovered at the end of the program, there has been no opportunity to study means of prolonging the resin life. Uncertainty concerning resin life makes the accurate prediction of costs impossible.

Several items of costs are omitted from the estimates. The disposal of the highly colored regenerant waste depends upon local circumstances. Unless the regenerant waste can be stripped of unwanted ions for reuse in the mill, it must be sewered, lagooned, pumped into deep wells or discarded in some other innocuous way. A truly acceptable means for the disposal of these wastes has not been found. The cost for modifying the process piping in an existing mill to accomodate an ion exchange plant and the added cost for extra piping in a new mill would depend upon the specific circumstances and is also omitted.

Ion exchange is a well-established process with a long history of successful commercial use. In spite of the seeming complexity of the equipment, ion exchange plants are reliable and can operate fully automatically with only about an hour of preventative maintenance and attention per day. In general, the life of the equipment may exceed

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15 years. However, an amortization period of 10 years at an interest rate of 9 percent is assumed herein.

DESALINATION AND COLOR REMOVAL FOR REUSE

Water Quality

The ranges in the desired properties of process water for reuse in kraft manufacture as given by Thibodeaux and Berger (1967) are reproduced in Table 28. The typical improvement to be expected in water quality obtained by ion exchange after massive lime precipitation is given in Table 29, but it should be emphasized that the figures are only typical and not absolute. The cation column was operated to a 35 percent breakthrough of the sodium ion which gave a high average leakage of 13 percent. In practice it might be desirable to operate to a higher leakage for greater efficiency or a lower leakage for improved quality. Furthermore, leakage is a complex function of several factors including regeneration level, relative concentration of ions, flow rates, rinse volume, countercurrent versus concurrent regeneration, and the design and operation of the reactor vessel. In general, leakage for the most economical operation of a simple cation-anion pair of reactors lies between about 8 and 20 percent for high solids feed. A second stage cation-anion pair could easily reduce the TDS to 20 mg/l and reduce the chloride to 10 mg/l.

The leakage from the first pair of reactors can be reduced in a number of ways. One means is to stop the run at a lesser throughput, although at some reduction of efficiency. Another is to add a layer of weak acid resin on top of the strong acid resin which transforms the simple cation reactor into a Duo-cat reactor described by Abrams and Poll (1967). The added cost consists only of the cost of the extra resin and a somewhat deeper reactor. Weak acid resin is lighter than strong acid resin and rises to the top during backwashing. The regenerating

TABLE 28

RANGES OF DESIRED PROPERTIES OF PROCESS WATER FOR KRAFT MANUFACTURE

Constituent	Unbleached	Bleached
Turbidity, mg/l	5-25	0-5
Color, CU	10-80	0-5
pH	6.5-8.0	6.8-7.3
Total alkalinity, mg/l $CaCO_3$	20-150	20-75
Hardness, mg/l $CaCO_3$	5-200	5-100
Dissolved solids, mg/l	50-500	50-250
Chloride, mg/l	10-150	10-150
Iron, mg/l	0.5	0.2
Manganese, mg/l	0.3	0.1
Chemical oxygen demand, mg/l	0-12	0-8
Biochemical oxygen demand, mg/l	0-5	0-2

TABLE 29

TYPICAL WATER QUALITY IMPROVEMENT BY ION EXCHANGE

	Typical Concentration After:			
Constituent	Massive Lime Precip, me/l	First Stage Ion Exchange, me/l	Approx Leakage, %	Second Stage Ion Exchange
Na+K	18.0-13.0	3.1	20	---
Ca	7.8-5.9	0	0	---
Mg	tr	0	0	---
HCO_3	5.3-4.3	0.1	2	---
Cl	17.2-12.9	2.4	16	---
NO_3	tr	0	0	---
SO_4	0.1-2.2	0	0	---
S	tr	0	0	---
Cations,	24.6-19.1	3.1	14	---
Total Anions	23.1-18.6	2.8	15	---
Total Mineral Acidity	18.5-13.4	2.8	17	---
TDS	1509-1209 mg/l	162 mg/l	12 mg/l	---
Color	300 CU	80 CU	27 CU	8 CU

acid must flow upward to contact the strong acid resin first. The weak acid resin is regenerated at nearly 100 percent efficiency even though the regenerant is both weak and contaminated. In the succeeding service cycle the weak acid resin removes cations up to the equivalence of the alkalinity. In bleach plant waste, alkalinity comprises 20 percent of the anions so the use of a Duo-cat reactor is feasible. Sanks (1968) found an overall efficiency of 72 percent in a cation reactor could be increased to 92 percent by the addition of 26 percent of weak acid resin. The leakage, originally 30 percent, was decreased to 16 percent. Another way to improve performance is to use a continuous, countercurrent ion exchange system (or an approximation, such as Progressive Mode) in which leakage is low and efficiency is typically 90 percent.

The raw waste quality varies considerably and the TDS after massive lime precipitation has varied from about 1100 to 1800. Some variation in quality of finished water can also be expected if the ion exchangers are operated on the basis of a preset time or volumetric basis. The reactors can, however, be operated on the basis of the quality of effluent to provide a nearly uniform product.

In summary, single stage operation can produce water adequate in quality for the manufacture of unbleached pulp. Water adequate in quality for bleached pulp manufacture can be produced by two-stage ion exchange and probably by single stage continuous counter-current ion exchange or by Progressive Mode. Decolorization to very low levels requires low pH, low leakage, and deep anion beds.

Estimated Cost for Single Stage Ion Exchange

The size of the reactors are based on the operating conditions given in Table 30. These in turn are based on the bench scale pilot plant

TABLE 30

OPERATING CONDITIONS FOR ION EXCHANGE

Item	Value
Cation Exchange	
Feed flow rate, BV/hr (ditch waste after massive lime precipitation)	20
Feed to breakthrough, BV of 19.1 me/l feed	33
Regenerant and rinse flow rate, BV/hr	16
Regenerant (3% H_2SO_4) volume, BV	1.30
Regenerant level, lb H_2SO_4/cu ft resin-cycle	2.43
Rinse volume, BV	3.00
Efficiency (me ions removed/me acid), %	75 (71-78)
Cycle time:	
Service, hrs	1.65
Backwash (every 6th cycle) per cycle, hrs	0.04
Regeneration, hrs	0.08
Rinse, hrs	0.19
Downtime (maintenance, repairs at 5%), hrs	0.10
Total cycle time, hrs	2.06
Cycles per day	11.65
Service volume per cu ft resin, gpd	2880
Total resin required, cu ft	1700
Water required for rinse and acid dilution, gpd	634,000
Acid required for 4,882,000 gpd, tons as H_2SO_4/day	24.0
Anion Exchange	
Feed flow rate, BV/hr	20
Feed to breakthrough, BV of 18.5 me/l Cl in feed	54
Regenerant and rinse flow rate, BV/hr	16
Regenerant (3% NaOH) volume, BV	1.30
Regenerant level, lb NaOH/cu ft resin-cycle	2.51
Rinse volume, BV	3.00
Efficiency (me ions removed/me base), %	85 (81-88)
Cycle time:	
Service, hrs	2.70
Backwash (every 6th cycle), hrs	0.04
Regeneration, hrs	0.08
Rinse, hrs	0.19
Downtime, hrs at 5%	0.15
Total cycle time, hrs	3.16
Cycles per day	7.59
Service volume per cu ft resin, gpd	3070
Total resin required, cu ft	1600
Water required for rinse and base dilution, gpd	390,000
Net product water, 4,882,000-634,000-390,000, gpd	3,858,000
Base required for 4,882,000 gpd, tons as NaOH	15.2

operations used in the laboratory. More extensive pilot plant experiment would result in obtaining more efficient operating conditions.

The capital equipment costs in Table 31 are based on the following conditions. Reactors are epoxy-lined mild steel equipped with multiport 304 stainless steel valves. Inlet and regeneration distributors are also of 304 stainless steel. Alkalinity is removed more cheaply by degasification than by ion exchange. Furthermore, weak base resins do not remove bicarbonate well. At times the feed water alkalinity has been as much as 350 mg/l as $CaCO_3$. To reduce this to 10 mg/l at 140°F requires 46 trays in a 12 ft x 12 ft x 16 ft high countercurrent degasification tower.

Regenerant storage, product storage, and process piping are omitted from the estimated capital cost of the ion exchange plant in Table 31. Regenerant might be stored in tank cars because, for such large amounts, there would be little or no demurrage. The requirements of product storage depend on the fluctuations of water use. Without fluctuations, there is no need for storage, and since unbleached pulp at the Hoerner Waldorf plant is made in a continuous Kamyr digester, little product storage is required. Some mills operating with batch digesters might require several hours of product storage. The cost of process piping depends upon the location of the ion exchange plant relative to the rest of the plant and an allowance for connecting the ion exchangers to the rest of the plant and is impractical to estimate. Furthermore, it would be entirely different for each mill, so an estimate would be merely speculative.

The costs of chemicals in Table 32 were taken from Tables 3 and 4. They are actual costs for chemicals delivered at the Hoerner Waldorf Mill, Frenchtown, Montana in April 1973. The cost for labor in Table 32 is uncertain. Ion exchange plants can operate at a minimum of labor despite the seeming complexity of the equipment. The charges

TABLE 31
ESTIMATED CAPITAL COST OF FIXED BED CATION-ANION EXCHANGERS

Item	Cost
Cation exchange: 8 reactors	
10 ft ID x 7 ft reactors with multiport valve control	--
1700 cu ft resin	--
4 inch automatic reset meters	--
Inlet regeneration distributors, 304 SS	--
100 psi code vessels	--
Automatic unit controls	--
2 sets if 4-unit system controls	--
Pipe and valves	--
2 sets H_2SO_4 regeneration systems	--
Skid mounted, piped, wired	--
Manufacturers engineering	--
Subtotal cation exchangers	310,440
Degasifier: Forced draft, fiberglass	
For reducing 350 mg/l alkalinity as $CaCO_3$ to 10 mg/l at 140°F	
12 ft x 12 ft x 16 ft high with 46 trays	24,000
Clearwell, buried 100,000 gal, neoprene lining	18,000
Supports and piping	8,000
Subtotal degasifier	50,000
Anion exchange: 8 reactors	
10 ft ID x 7 ft reactors with multiport valve control	--
100 psi code vessels	--
1600 ft^3 resin	--
8 conductivity meters	--
Inlet and regenerant distributors, 304SS	--
Automatic unit controls	--
2 sets 4-unit system controls	--
Interconnecting piping and valves	--
2 sets NaOH regeneration systems	--
Skid-mounted, piped, and wired	--
Manufacturers engineering	--
Subtotal anion equipment	365,560
Building and foundations, 162 x 48 at $18/sq ft	84,480
Feed pump, rubber covered, 4 @ 1700 gpm and 20 hp motors	18,000
Total equipment cost	829,280
Engineering at 10% total equipment cost	82,928
Erection and hook-up at 10% total equipment cost	82,928
Contractor's profit and overhead at 12% equipment + erection	109,465
Freight: cation, anion, degasifier	43,000
Start up	5,000
Total capital cost excluding storage and process piping to ion exchangers	1,152,601
Capital cost per gallon of product (3,858,000 gal)/day	0.30

for amortization may or may not be realistic. Amortization periods in industry rarely exceed 7 years and interest rates are often more than 9 percent. On the other hand, the equipment life is probably in excess of 15 years. But combining life and amortization periods into one value, 10 years, is not far amiss and avoids complex cost analyses.

The operational costs shown in Table 32 and in the first line of Table 33, are based on a resin life of 12 months and if the aggressiveness of the wastewaters can be reduced to permit resins to last a year, the costs shown are reasonable. Abrams (1973) stated there are several ways to reduce the attack on resins including: treatment of feed with sulfur dioxide or (occasionally) with sodium hydrosulfite, cold temperature, and use of weak regenerants. Pretreatment by Amberlite XAD-8 can give colorless feeds, but its effect on aggressiveness is quite unknown. If the life of the resin cannot be prolonged, the resins must be replaced every 2 months, and the costs would be increased to $1.38/1000 gallons as shown in line 2 of Table 33.

The water required for dilution of regenerants and for rinsing and backwash need not, necessarily, be product water. For this economic analysis, it was assumed regenerant dilution water and rinse water was product water and backwash water was feed that could be reused in the process. The quantities used are given in Table 30. The most economical operating conditions require considerably more investigation. Acid and base dilution water cannot be reduced greatly, but 3 BV of rinse is much more than is required. In previous work with waters containing higher TDS than bleach plant effluent Sanks and Kaufman (1965) found rinse volumes of 1.3 BV to be adequate and this lower rinse requirement would reduce costs to $1.24/1000 gallons as shown by line 3 of Table 33.

TABLE 32
OPERATING COSTS FOR SINGLE STAGE ION EXCHANGE

Item		Cost $/Day
Electric power at 1¢/kw hr		11.58
Sulfuric acid, 24 tons H_2SO_4 at $25.37/ton, 75% efficiency		608.88
Caustic, 15.2 tons NaOH at $67.45/ton as 50% Na_2O, 85% efficiency		1589.52
Maintenance at 0.0075% equipment cost		62.20
Taxes and insurance at 0.006% capital cost		69.16
Cation exchanger, 100% replacement/year		116.44
Anion exchanger, 100% replacement/year		284.93
Operating labor		
1 hr supervision/day at $7.50/hr	7.50	
4 hrs labor/day at $6.00/hr	24.00	
Benefits at 15%	4.73	
Overhead at 50%	18.12	
Contract 16 hrs/month instrument service at $20.00/hr	10.52	
Subtotal	2807.58	2807.58
Amortization, 10 yrs at 9% interest		492.05
Total		3299.63
Total cost, $/1000 gal net product (3,858,000 gpd)		0.86
Total cost, $ per ton bleached pulp (150 tons/day)		22.00

TABLE 33
COST VERSUS OPERATING CONDITIONS OF SIMPLE ION EXCHANGE

Conditions						
% Acid Efficiency	Base	% Base Efficiency	Rinse, BV	Product, % of Feed	Resin Life, Months	Cost, $/1000 gal of net product
75	Caustic	85	3	79	12	0.86
75	Caustic	85	3	79	2	1.38
75	Caustic	85	1.3	87	2	1.24
90	Ammonia	85	1.3	87	12	0.48
90	Ammonia	85	1.3	87	36	0.42

The cost of base is the largest item because caustic is very expensive. Other possibilities for reducing the regenerant cost include: the integration of spent regenerant into the mill process to eliminate waste, the use of lime, and the use of ammonia with or without ammonia recycle by recovery with lime. The integration of spent regenerants with mill processes was not pursued in this investigation due to lack of time and financial resources. Certain difficulties can be foreseen such as the high concentration of chlorides and the separation of other ions, but the rewards of success are so great that serious efforts should be made to overcome these difficulties. Lime was not an effective regenerant with Duolite A-6 resin as shown in Figure 76, but on the other hand only limited efforts were made to optimize lime regeneration. Odland and Pabich (1965) reported successful, low-cost regeneration of strong base resins with lime in the Sul-biSul process but only when the SO_4/Cl ratio was 9 or more. Low sulfate water, such as ditch waste, is not suited to the Sul-biSul process according to Schmidt et al (1969).

Time ran out before cyclic runs could be made with ammonia as the regenerant, so the sustained efficiency is unknown. In a single run, however, regeneration with ammonia was 80 percent as effective as regeneration with caustic as Figures 77 and 78 show. With optimization ammonia regeneration efficiency could be increased to at least 85 percent. At the delivered cost of $70/ton quoted by Whaley (1973) for anhydrous ammonia, the cost of ammonia is 28 percent of the cost of caustic on a pound-equivalent basis. Hence, the daily cost for anion regeneration with ammonia would be about $452/day which would reduce the demineralization cost to $0.48/1000 gallons assuming a 12-month resin life and the regeneration efficiencies (shown in Table 33) previously determined by Sanks and Kaufman (1965) and by Sanks (1967).

The recovery of ammonia with lime is a well-known process, but it would require careful investigation to determine whether such an operation would be economical. If resin life can be increased to three years, the cost of ion exchange would be reduced to $0.42/1000 gallons assuming: ammonia for base regenerant, Duo-cat cation columns, and optimum operating conditions with respect to flow rate, regeneration level, and rinse volume.

Estimated Cost for Progressive Mode System

Any of the continuous countercurrent ion exchange systems (Chem-Seps or Graver and their approximations) possess the advantages of low leakage combined with highly efficient regeneration. The Progressive Mode system closely approximates continuous countercurrent ion exchange, the efficiency is good, the leakage is low, and it possesses distinct advantages in versatility. The operation can be changed in the field and at will by altering the timer settings. It can even be operated as a simple single stage cation-anion system. Its disadvantages are the complexity of operation which requires an expert to adjust the timers and the high head loss resulting from the high flow rates employed. As neither disadvantage is serious, a comparison of Progressive Mode with simple ion exchange is illuminating.

The capital equipment costs shown in Table 34 are based on the same considerations as the capital equipment costs in Table 31. To protect the Permutit Company, the costs of individual items are omitted in favor of a total sum.

Because pilot plant experience and optimization are not available, the operating costs of Progressive Mode ion exchange are somewhat uncertain. However, acid and base regeneration efficiencies are higher than in simple fixed-bed cation-anion pairs and on the basis of experience with other installations it appears likely that regeneration efficiencies of approximately 87 percent can be realized. Accordingly acid and base quantities of 115 percent of cations and (except for alkalinity) anions were used for the operating cost estimates in Table 35.

TABLE 34

ESTIMATED CAPITAL COST OF A PROGRESSIVE MODE ION EXCHANGE SYSTEM

Item	Cost, $
Cation reactors: 2 trains of 4 units	
8 ft ID x 10 ft reactors with valve nest	---
1700 cu ft resin	---
8 sets inlet and regeneration distributors 304SS	---
100 psi code vessels	---
Automatic controls for 2 4-unit trains	---
Interconnecting piping and valves	---
2 - H_2SO_4 regeneration systems	---
Skid mounted, piped, and wired	---
Manufacturer's engineering	---
Subtotal cation exchangers	$ 310,440
Degasifier (See Table 30)	50,000
Anion reactors: 2 trains of 4 units	
8 ft ID x 10 ft reactors with valve nest	---
100 psi code vessels	---
1600 cu ft resin	---
8 sets inlet and regeneration distributors 304SS	---
Automatic controls for 2 4-unit trains	---
Interconnecting piping and valves	---
2 - NaOH regeneration systems	---
Skid mounted, piped and wired	---
Manufacturer's engineering	---
Subtotal anion exchangers	365,560
Building and foundations	84,480
Feed pumps	23,000
Total equipment	833,480
Engineering at 10%	83,348
Erection and hook-up at 10%	83,348
Contractors profit and overhead at 12% equipment and erection	110,019
Freight: cation, anion, degasifier	43,000
Start up	8,000
Total capital cost except for storage tanks, and process piping to ion exchanger	1,161,195
Capital cost per gallon product (4,265,000 gal)/day, $	0.27

TABLE 35

OPERATING COSTS FOR PROGRESSIVE MODE ION EXCHANGE

Item		Cost $/day
Electric power at 1¢/kw hr		19.69
Sulfuric acid, 20.7 tons H_2SO_4 at $25.37/ton, 87% efficiency		525.16
Ammonia 6.31 tons NH_3 at $70/ton, 87% efficiency		441.70
Maintenance at 0.0075% equipment cost		62.51
Taxes and insurance at 0.006% capital cost		69.67
Cation exchanger, 100% replacement/year		116.44
Anion exchanger, 100% replacement/year		284.93
Operating labor		
7 hrs supervision/week at $7.50/hr	7.50	
4 hrs labor/day at $6.00/hr	24.00	
Benefits at 15%	4.73	
Overhead at 50%	18.12	
Contract 16 hrs/month instrument service at $20/hour	10.52	
Subtotal	1584.97	1584.97
Amortization, 10 yrs at 9 percent		495.72
Total		2080.69
Total cost, $/1000 gal net product (4,265,000 gpd)		0.49
Total cost per ton bleached pulp (150 tons/day)		13.87

Careful attention to details can reduce the rinse and regenerant dilution water requirements to 13 percent of the total feed thereby producing a net product of 4,265,000 gpd, and these are the values used in Table 35.

Again, the cost of desalination is greatly dependent on replacement of resin, labor and amortization. If resins must be replaced six times per year, the desalination cost will be increased approximately to $0.96/1000 gal. On the other hand if the aggressiveness of the feed water can be decreased sufficiently, cation and anion resins should last three years, which would reduce the cost to $0.43/1000 gal.

COLOR REMOVAL

Color removal from kraft bleach wastes at the pH ranges encountered in the Hoerner Waldorf Mill was not notably successful. At the low pH (about 2.2) of decationized waters, color removal was successful when combined with anion exchange. Because complete (or nearly complete) color removal without desalination was not obtained, cost estimates for color removal without desalination are not warranted at the present stage of development.

The Rohm and Haas Company (1973) reported 78 percent reduction in color from a bleach plant waste stream consisting of equal parts of caustic extraction liquor and chlorine stage liquor at an estimated cost of 3.5¢/1000 gal or $0.84/ton pulp for treating 5 mgd from a plant producing 800 tons of bleached pulp per day. Rubber-lined steel vessels and maintenance and repair were included in the cost estimates. Labor was excluded. The life of Amberlite XAD-8 resin assumed to be 5 years. The amortization was based on a 20 year life at 5 percent interest. The total capital cost was $1,300,000 including filtration and all process piping. Of course, greater color reduction can be achieved but at a higher cost.

During the final stages of preparation of this manuscript, Anderson, Broddevall, and Lindberg (1973) reported success after many years of experimentation in decoloring bleach plant effluents by ion exchangers. They were able to decolor caustic extract stage liquor completely. However, with more conservative practice (allowing 35 percent color breakthrough at the end point) color was reduced by 96 percent, COD was reduced by 90 percent, and BOD was reduced by 60 percent. The resin was regenerated by black liquor and the eluant was then burned in the recovery furnace. The capital cost of a plant for treating the caustic extract stage of a 300 ton per day bleach plant was estimated to vary from $500,000 to $1,000,000. Kamyr, Inc. is marketing the method in North America. Such a process might well be incorporated into desalination by ion exchange.

PRETREATMENT

None of the costs yet discussed include pretreatment. Wright (1972) stated the cost for massive lime precipitation might be as high as $1.80/ton of pulp which would increase the total cost in Table 35 to $15.67/ton of pulp or $0.56/1000 gal. Pretreatment by ion exchange using the Rohm and Haas Company (1973) method with Amberlite XAD-8 resin would certainly cost more than $0.035/1000 gallons but it might well replace massive lime precipitation. Furthermore, as pretreatment by XAD-8 removes compounds causing color, it may also remove other substances that attack the resins used for desalination. The ion exchange method of Anderson, Brocdevall, and Lindberg (1973) might also be used in place of massive lime precipitation for pretreatment preceeding desalination. The necessity for further pretreatment for such as filtration has not been determined. A large pilot plant operating at the mill for an extended period of time would afford the best basis for this judgment.

COMPARISON WITH REVERSE OSMOSIS

The only serious competitor with some form of the ion exchange process appears to be reverse osmosis. Extensive research over a number of years by Wiley, Dubey, and Bansal (1972) culminated in predicted capital costs of $0.82 to $1.48 per daily gallon of permeate water for plants producing 0.1 mgd to 1 mgd of kraft bleach effluent. Total operating costs were estimated at $1.32/1000 gallons of product water. The use of improved membranes (which apparently became available too late for testing) might reduce capital and operating costs to $0.58 per daily gallon and $0.82/1000 gallons of product water respectively.

Cost comparisons are frought with uncertainties. Amortization periods, interest rates, chemical prices, life of equipment, labor, pretreatment, waste disposal, integration of the process into the rest of the plant, bias of the estimator, and other factors all contribute to the uncertainty. But it has been shown, under conditions of the actual testing, the cost of ion exchange is about the same as the cost of reverse osmosis. Under the best conditions, the speculative cost of ion exchange is about $0.43/1000 gallons compared with $0.82/1000 gallons for reverse osmosis. These figures are based upon different assumptions concerning life, interest, plant hook-up, pretreatment, waste disposal, etc., and therefore they are not directly comparable. Whether ion exchange will eventually prove to be less costly in full scale plants depends on the solution of pretreatment problems, the life of membranes and resins, the relative costs of waste disposal and the ease of integration into the pulp mill facilities. But in any event it is safe to conclude ion exchange is competitive and the method deserves more research effort to bring it into focus with reverse osmosis.

SECTION IX

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SECTION X

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SECTION XI

GLOSSARY

ALKALINITY	The buffering capacity of water. Specifically, it is $CO_3 + HCO_3 + OH - H$. Also it includes other weak acid anions such as borates, silicates, and phosphates. It is expressed in milligrams per liter of equivalent calcium carbonate or in milliequivalents.
ANION	A negatively charged ion in solution attracted to the anode under the influence of electric potential.
BACKWASHING	The operation of cleansing a resin bed by an upward flow of water sufficient to expand the bed and aggitate the particles. Backwashing reclassifies the bed so lighter, smaller particles are lifted to the top. Channels formed during the service cycle are eliminated which promotes uniform flow in the following service cycle.
BED DEPTH	The effective height of resin in the reactor.
BED EXPANSION	The added height to which resin rises during backwashing expressed as a percentage of the unexpanded bed depth.
BED VOLUME (BV)	The total volume of the resin particles plus the pore volume between particles in the unexpanded bed.
BV/hr	Flow rate expressed as bed volumes per hour.
BIOCHEMICAL OXYGEN DEMAND (BOD)	The quantity of oxygen used in the oxidation of organic matter by bacteria under standard conditions of temperature, time, quiescence, and absence of light. It is a measure of readily oxidizable organic material.
BLACK LIQUOR	The product of white liquor after being used to digest wood chips. It contains less caustic, more carbonates, and large quantities of lignin. This black fluid is burned for the recovery of chemicals and when the ash is redissolved the resulting fluid is called green liquor.

BOD-5	Biochemical oxygen demand over a five day period at 20°C.
BREAKTHROUGH	The rapid increase in the concentration of an ion or color in the effluent. It is expressed as a percentage of the concentration of the substance in the feed water.
CALCIUM CARBONATE EQUIVALENT ($CaCO_3$)	A means for expressing the number of equivalents of a constituent in terms of an equivalent weight of calcium carbonate commonly used for ease in calculation and elimination of ambiguity. 50 mg/l $CaCO_3$ = 1 equivalent.
CAPACITY	The amount of ions that can be held by a resin. It is usually expressed as kilograins (as calcium carbonate) per cubic foot, but it can also be expressed in other ways. For example, 1 me/ml = 21.85 kilograins per cubic foot.
CATION	A positively charged ion which migrates to the cathode in a solution.
CAUSTIC EXTRACT	A stage in the bleaching process. Waste from this stage contains much more color than wastes from other stages.
CHEMICAL OXYGEN DEMAND (COD)	A measure of the organic material in water in terms of its oxygen-consuming capacity when subjected to boiling in acid solution with an excess of a strong oxidant.
cm	Centimeter.
COLOR UNIT (CU)	A measurement of the intensity of color compared to a standard solution of 1 mg/l Pt in the form of chloroplatinate ion augmented with 0.5 mg $CoCl_2$ as Co.
CU-liter	The quantity of color in one liter at a concentration of 1 CU.
CONCURRENT	Operation of an ion exchange bed in which direction of flow in the service cycle is the same as the direction of flow of the regenerant.

COUNTERCURRENT	Operation of an ion exchange bed in which the direction of flow during the service cycle is opposite to that of the regenerant.
CONDUCTIVITY	The ability of water to conduct electricity expressed in the reciprocal of resistance as micromhos/square centimeter or, more simply μmhos.
Cwt	Weight expressed in hundredths of pounds.
DECATIONIZATION	Ion exchange with a cation resin in which the cations are replaced by hydrogen ions.
DEMINERALIZATION	The removal of the mineral content of water. It can also mean reduction of the mineral content.
DESALINATION	The partial removal of salts from water by physical or chemical means.
DITCH WASTE	In this report, ditch waste is the aggregate waste leaving the bleach plant. It consists of approximately 15 percent caustic extract, 85 percent chlorination stage effluent, minor spills, floor sweepings from the lime kiln area, and sporadic flows of black liquor.
DUO-CAT	A layer of weak acid cation resin on top of a bed of strong acid cation resin. The combination of the advantages of both resins produces low leakage plus high efficiency in regeneration.
EFFLUENT	The liquid that emerges from a reactor or a tank.
ELUTION	Removal of sorbed ions from an ion exchanger by regeneration with concentrated chemical solutions. The regenerant solution is the eluant. The effluent is the eluate.
EQUIVALENT (eq)	An amount of substance equivalent to one mole of hydrogen ions.
ENDPOINT	The end of the service cycle defined as some desired percentage of breakthrough.

EXCHANGER	Any substance, such as ion exchange resins, sulfonated coal, or zeolite which can reversibly exchange one ion for another.
EXHAUSTION	Exhaustion and service are synonymous. That part of the service cycle in which feed is pumped through the resin bed. The resin is exhausted at the endpoint.
FEED	The solution introduced into a reactor.
FIXED-BED	An ion exchange system in which the resin does not leave the reactor. Temporary disturbances of the bed by backwashing does not alter its status as a fixed-bed reactor.
HOOK-UP	Connect, join, or attach any device, reactor or pump to the remainder of the plant.
ID	Internal diameter.
INFLUENT	Synonymous with feed. The solution introduced into a reactor or tank.
JTU	APHA Jackson Turbidity Units. A measure of turbidity.
LEAKAGE	The unsorbed ions present in the effluent.
LIME	In general, any of a family of chemicals composed of calcium and sometimes containing magnesia. In this report, lime which is dry is CaO, and lime in water is $Ca(OH)_2$.
LIFE TEST	Continuous cyclic tests of exhaustion and regeneration in rapid sequence to determine the degradability of resins. The "life" of a resin is its operating period during which it retains sufficient physical and chemical integrity for use.
me/l	Milliequivalents (1000th of an equivalent) per liter.
MICROMHOS (μmho)	Electrical conductivity equal to 1 millionth of a reciprocal ohm.

MOVING BED	In moving bed reactors, resins are pumped from one portion of a reaction into another portion of the same reactor or into a different reactor for different parts of the service cycle such as exhaustion, regeneration, and rinse.
NORMAL (N)	A concentration of acid of base equal to one equivalent per liter.
OD	Outside diameter.
PLENUM	The space between the top of the resin bed and the top of the reactor.
ppm	Parts per million and approximately equal to mg/l.
PRODUCT	The finished water or effluent from an ion exchange system.
PRODUCT RECOVERY	The product remaining after utilization of some of the feed for acid and base dilution and rinse.
REGENERANT	The chemical solution used to restore the exchange capacity of a resin. Also eluent.
REGENERATION	The portion of the service cycle in which the regenerant flows through the resin bed.
REGENERATION EFFICIENCY	The milliequivalents of ions eluted from the resin divided by the milliequivalents of ions supplied in the regenerant and usually expressed as a percentage. See true and superficial efficiency.
RINSE	The part of the service cycle in which regenerant in the reactor is displaced by water, usually product water.
SALT SPLITTING	The conversion of neutral salts to their corresponding acids or bases.
SELECTIVITY	The preference of a sorbent for one ion over another. It is a function not only of the resin itself but of the absolute and relative concentrations of ions in the solution.

SERVICE	The part of the ion exchange cycle in which feed is converted to product.
STARVATION REGENERATION	Regeneration in which small amounts of chemicals are used in order to increase regeneration efficiency.
STRONG ACID RESIN	A cationic exchanger with strong acid functional groups such as sulfonic acid. Such exchangers exhibit high selectivity for other ions over hydrogen ion and will operate in a pH range of less than one to 14.
STRONG BASE RESIN	An anion exchanger with strongly basic functional groups such as quaternary ammonium. Such exchangers exhibit high selectivity of other ions over OH and can operate in any pH range from 0 to 13.
SUPERFICIAL EFFICIENCY	Milliequivalents of ions eluted from resin divided by milliequivalents of ions in the regenerant.
THROUGHPUT	The amount of feed that passes through a resin bed, usually expressed in bed volumes.
TOTAL ORGANIC CARBON (TOC)	The concentration of organic carbon found by oxidizing the carbon at high temperature in a stream of pure oxygen aided by a catalyst.
TDS	Total dissolved solids
tr	Trace. It indicates the presence of a chemical in quantities smaller than is convenient to tabulate or to measure.
TRUE EFFICIENCY	Milliequivalents of ions sorbed from the net, useable product water divided by milliequivalents of ions in the regenerant.
WEAK ACID RESIN	An exchanger containing weak acid functional groups such as carboxylic acid. Such exchangers cannot split strong electrolyte salts such as sodium chloride but can split salts of weak acids such as sodium bicarbonate. They can operate between pH 5 and 14.

WEAK BASE RESIN	An exchanger containing weak base functional groups such as primary, secondary, or tertiary amines. Such exchangers can only operate between pH 0 and pH 7 or 8.

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